농학박사학위논문

GC-MS/MS와 LC-MS/MS를 이용한 농식품 중 500개 잔류 농약 성분의 다성분 신속동시 분석 연구

Simultaneous and Rapid Analysis of 500 Pesticide Multiresidues in Agricultural Products Using GC-MS/MS and LC-MS/MS

2017년 8월

서울대학교 대학원

농생명공학부 응용생명화학전공

이 종 화

A Dissertation for the Degree of Doctor of Philosophy

Simultaneous and Rapid Analysis of 500 Pesticide Multiresidues in Agricultural Products Using GC-MS/MS and LC-MS/MS

August 2017

Jonghwa Lee
Applied Life Chemistry Major
Department of Agricultural Biotechnology
Seoul National University

Abstract

A multiresidue method for the simultaneous and rapid analysis of 500 pesticides in representative agricultural produce (brown rice, orange, spinach, and potato) was developed using a modified QuEChERS procedure combined with gas and liquid chromatography–tandem mass spectrometry (GC-MS/MS and LC-MS/MS). Multiple reaction monitoring parameters (e.g., collision energy, precursor and product ions) in MS/MS were optimized to achieve the best selectivity and sensitivity for a wide range of GC or LC-amenable pesticides. For the GC analysis of 360 pesticides, a short (20 m) microbore (0.18 mm i.d.) column resulted in better signal-to-noise (S/N) ratio with reduced analysis time than a conventional narrowbore column. The use of pulsed pressure injection was also effective to increase the peak response and S/N ratio. After changing a new liner, the priming injection, which caused by masking effect was suggested in order to consistent peak sensitivity. In LC-MS/MS analysis of 332 pesticides, the optimal mobile phase and injection volume was evaluated to acquire high sensitivity and reliable results. The limit of quantitation was <0.01 mg/kg, and the correlation coefficients (r^2) of matrix-matched standards were >0.99 within the range of 0.0025–0.1 mg/kg. Acetonitrile with 0.1% formic acid without additional buffer salts was used for pesticide extraction, whereas only primary–secondary amine was used for dispersive solid phase extraction cleanup, to achieve good recoveries for most of the target analytes. The method was validated according to the European Union SANTE guidline.

The recoveries ranged from 70 to 120% with relative standard deviations of ≤20% at 0.01 and 0.05 mg/kg spiking levels (n = 6) in all samples, indicating acceptable accuracy and precision of the method. The results of matrix effects

were indicated that mainly signal enhancements were observed in GC-MS/MS but in the LC-MS/MS, the evenly spread across the ranges and little difference within the samples. The optimized method was successfully applied to the analysis of pesticide residues in real samples.

Key Words: **apple, brown rice, GC-MS/MS, LC-MS/MS, orange, pesticide multiresidues, potato, QuEChERS, spinach**

Student Number: **2013-30354**

Table of Contents

Part 1 : Rapid and Simultaneous Analysis of 360 Pesticides in Crops Using Microbore GC-MS/MS

List of Tables

List of Figures

Introduction

Introduction to pesticide multiresidue analysis

Pesticide residue level of agricultural produce is one of the most important issues because it is directly related with human health safety. In addition, regulating pesticides among countries around the world is sensitive issue since different countries have different regulations, requirements and permissible limits in terms of pesticides residue. To ensure that levels of pesticide residues on grains, fruits, and vegetables meet current tolerances or maximum residue limits (MRLs) of individual countries, they are strictly monitored by authorities. Considering that new agrochemical pesticides are introduced to the market each year, they must be strictly evaluated by governments to make sure that they meet current health, environment and safety standards before the new products are available to farmers. Therefore, the rapid and effective analytical methods, multiresidue pesticide screening can play a significant role in mornitoring the unknown pesticides in imported or exported food matrices (i.e. vegetables, fruits and meat).

Pesticide multiresidue analysis is a procedure of the identifying and quantifying the several or hundreds of pesticide residues at the same time. It is a notoriously difficult, laborious and time-consuming work to ensure the accuracy and reliable data, detecting very low levels of pesticides in various sample matrices. Because a large number of pesticides potentially has been used during the harvest of agricultural produce, the development of multiresidue methods, which can provide quantitative and qualitative information simultaneously for many compounds is required. (Tsipi et al., 2015).

Instrumental analysis in pesticide multiresidue

Conventional gas chromatography (GC) and high performance liquid chromatography (HPLC) have several limitations in fast and simultaneous multiresidue analysis. Extensive partitioning and cleanup procedures are also required to remove coextractives for baseline separation of peaks on GC or HPLC, often causing low recoveries and precisions by loss of analytes.

Mass spectrometry (MS) could be contributed for qualitative and quantitative analysis by specific fragmentation because it could overcome the drawback of conventional instrumental methods such as GC-ECD, NPD, or HPLC. In the screening, identification, and quantification of complicated organic pollutant, the combination of chromatography and MS has become one of the powerful tools (Lin et al., 2009).

GC or LC combined with tandem mass spectrometry (MS/MS) has played a vital role recently in monitoring multiresidue pesticides in food matrices. Multiple reaction monitoring (MRM, operating as “molecular cleanup”) by MS/MS enables the simultaneous analysis of hundreds of pesticides (Alder et al., 2006; Rajski et al., 2013) in a short time with high sensitivity and selectivity. Gas chromatography mass spectrometry (GC–MS) is mainly used for relatively volatile, non-polar, and thermally stable compounds (Lin et al., 2009). On the other hand, liquid chromatography mass spectrometry (LC–MS) is useful for nonvolatile, thermal unstable, and polar compounds without derivation. This paragraph describes recent advances in MS/MS including principle of tandem mass spectrometry, GC-MS/MS, and LC-MS/MS.

Principle of triple quadrupole-mass spectrometry

Mass spectrometry (MS) can separate organic molecules according to their molecular weight and enable its detection with high sensitivity. It is not only regarded as having good selectivity, but also a very sensitive instrument. The principle of the MS/MS technique is illustrated in **Figure 1**. The mass spectrometer aim to boost the detection of low amounts of target compounds, while also to identify the species corresponding to each chromatographic peak through its unique mass spectrum (Sargent [ED], 2013).

A triple quadrupole (TQ) mass spectrometer, is a kind of tandem mass spectrometer that is consisted of two mass analyzers of quadrupole type. with a collision cell. Tandem mass spectrometry, also known as MS/MS or MS^2, involves multiple steps of mass spectrometry selection, with some form of fragmentation occurring in between the stages (IUPAC, 1997). This configuration is often abbreviated Q1, Q2, and Q3. As seen in **Figure 2**, the first and third quadrupoles act as a mass filters, while the second quadrupole fragment the precursor ion using a collision gas (usually N_2 or Ar) (Banerjee and Utture, 2015).

Essentially, the triple quadrupole mass spectrometer is operated under the same principle with the single quadrupole mass analyzer. The quadrupole analyzer has capability to detect and measure the abundance of target ions. These gases, pass through the electrically connected four parallel, cylindrical metal rods (quadrupole) in order to reach the detector. The radio frequency (RF) potential associated with the collision cell allows all ions that were selected for to pass through the quadrupole (Dass, 2007). In some instruments, the normal quadrupole collision cell has been replaced by hexapole (Kaplan et al., 2008; Rostom et al., 2000) or octopole collision cells (Håkansson et al., 2003) in order to improve efficiency.

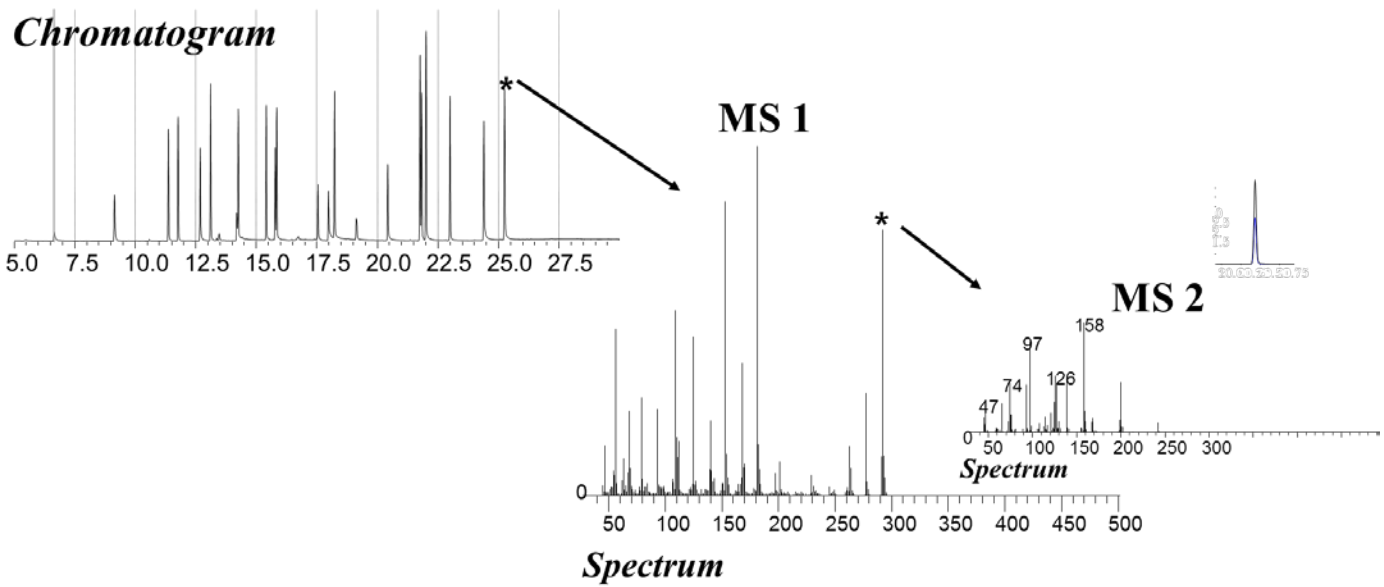
Unlike single MS instruments, MS/MS techniques allow for mass analysis to occur in a sequential manner in different regions of the instruments. The TQ enable in accordance with the structurally continuous arrangement, due to ionization, primary mass selection, fragmentation by collision induced dissociation (CID), mass analysis of fragments, and detection occurring in separate segments of the instrument (Johnson et al., 1990). In addition, the triple quadrupole mass spectrometer has many advantages including cheaper price (cheaper than two individual single quadrupole instruments), easy to operate, and they are highly efficient (Dass, 2007).

In MS/MS, the main function are scanning of product ions, precursor ion, neutral loss, selected reaction monitoring (SRM), and multiple reaction monitoring (MRM), as well as single Q1 or Q3 scan. Banerjee and Utture (2015) described the operating principle each scan mode as follows. ***The product ion scan mode***: A specific ion which will be fragmented in Q2 (collision cell) is selected in the first quadrupole (Q1). Then, the third quadrupole (Q3) scan the all *m/z* range with given spectrum and information on the sizes of the fragmented ions. At this time, the specific fragmentation patterns appear depends on the collision energies. Most abundant product ion and the CID voltage are generally chosen for quantitation. ***The precursor ion scan mode*****:** certain product ion is fixed in Q3, and the precursor masses, which can produce the product ion are scanned in Q1. ***The neutral loss scan***: both Q1 and Q3 are scanned together, but with a constant mass offset. This allows the selective recognition of all ions, which, by fragmentation, leads to the loss of a given neutral fragment (e.g., H_2O, NH_3). ***SRM/MRM***: In this method, both Q1 and Q3 are set to a selected ion, allowing only a distinct fragment ion from a certain precursor ion to be detected. This method results in increased sensitivity. If more than a single mass are set for Q1 and/or Q3, this configuration is called

MRM. When triple quadrupole is operated with MRM mode, the simultaneous detection in a low level of concentration in a one run is possible.

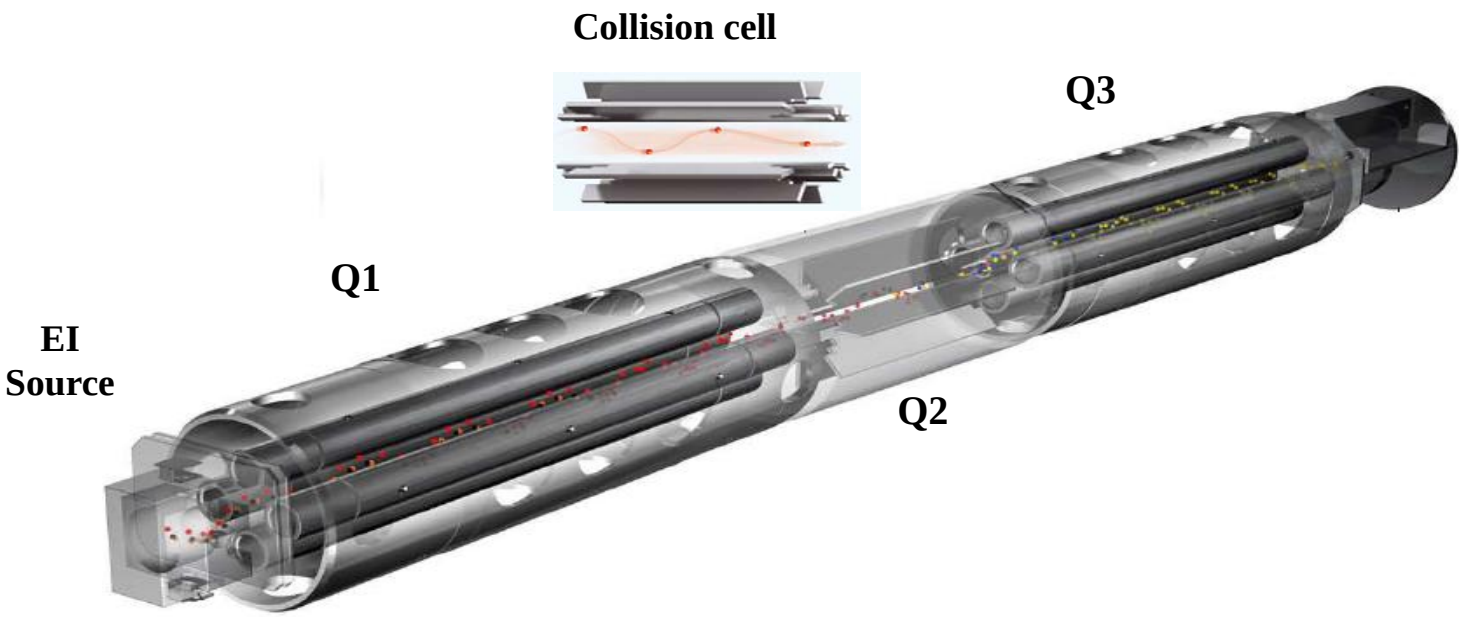
During the last decade, GC and LC–MSMS triple quadrupole mass spectrometer have become the standard for quantitative multiresidue methods for the analysis of pesticides and other residues. The main benefits of triple quadrupole are increased selectivity, improved signal-to-noise (S/N) ratio, lower limits of quantitation (LOQ), and improved accuracy. The triple quads have gained their popularity due to the increased scan speed and robustness of the instruments, allowing the simultaneous detection of several hundreds of analytes in routinely analysis.

Figure 1. The principle of the MS/MS technique separating and identifying by the fragmentation


Chromatogram
5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 25.0 27.5
MS 1
0
50 100 150 200 250 300 350 400 450 500
Spectrum
MS 2
158
97
126
74
47
0
50 100 150 200 250 300
Spectrum

5

Figure 2. Main scheme of triple quadrupole in GC-MS/MS (www.shimadzu.com).


Collision cell
Q3
Q1
EI
Source
Q2

Gas chromatography-triple quadrupole mass spectrometry (GC-MS/MS)

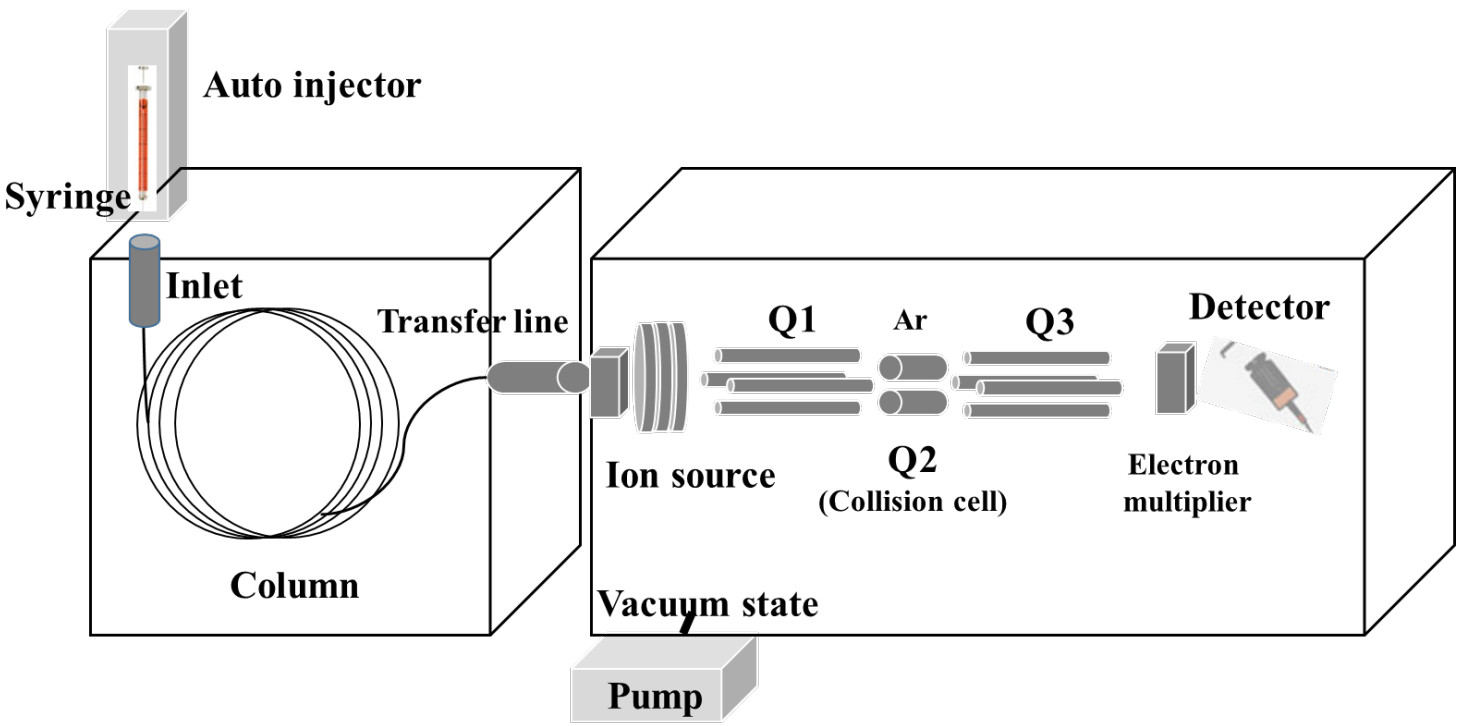
It is necessary to separate the target analyte from the matrix components, which is containing thousands of other different molecules. Gas chromatography (GC) has been widely used to separate the target compounds from food matrices. Not long ago, most pesticide residue analysis using GC has been used in combination with electron captured detector (ECD), nitrogen phosphorous detector (NPD), and flame ionization detector (FID). This combination of detectors has been contributed as a popular instrumental configuration for analysis pesticides in laboratories that are not equipped with MS (Aysal et al., 2007). GC in itself, has powerful separation performance due to the relatively narrow and sharp peak shape, allowing the easy identification and measurement for the individual compounds. Even though these conventional techniques have been considered as specific detection, the confirmation of results is limited due to the matrix interference and needs for multiresidue analysis.

Recently, it is well known that the development of MS technique could provide higher sensitivity and selectivity for pesticide analysis. Simultaneous determination and confirmation of pesticide residues could be achieved by GC equipped with tandem mass spectrometry (MS/MS) in one analytical run, which improves the analytical accuracy and shortens the analytical time (Lin et al., 2009). **Figure 3** shows structure of general GC-MS/MS. After separation by gas chromatography, the anaytes continues to enter the mass spectrometer. The analyts particles are then ionized by a variety the type of mass spectrometer such as EI, CI or NCI. The ionized anaytes has specific fragmentation patterns, out of fragmented ions, the precursor ion is selected in Q1. The selected (filtered by radio frequency) precursor ion undergo one more fragmentation by collision energy (eV) in collision cell/Q2. The produced (or fragmented) ion is called to product ion, then specific product ion is filtered again in Q3. Most of MS

analyzers can be used to consist a tandem mass spectrometry, the use of MS/MS has been already introduced in routine analysis of pesticide residues.

For the GC analysis, a narrowbore (0.2 mm ≤ i.d. < 0.3 mm)(Mastovská and Lehotay, 2003) column such as a 30-m column with 0.25 mm i.d. has been widely used for the separation of various pesticides. However, it generally requires a >30 min run time for one sample. For faster analysis, a low pressure-GC method uses a short megabore column (e.g., 10 m × 0.53 mm i.d.) for multiresidue analysis with the advantage of large sample loading capacity, but it requires an additional restriction column to maintain positive pressure in the inlet. In addition, the negative influence on the vacuum state of the mass spectrometer caused by the large volume of carrier gas flow may give rise to increased detection limit (Rossi et al., 1992). On the other hand, a microbore column (0.1 mm ≤ i.d. < 0.2 mm) has not been widely studied for the fast and simultaneous analysis despite its good performance with higher signal-to-noise (S/N) ratio (Mastovská and Lehotay, 2003). The column also provides increased efficiency and higher sensitivity by reducing resistance to mass transfer (Banerjee and Utture, 2015). Furthermore, it can provide enough linear velocity with low carrier gas flow for narrow chromatographic bands. However, it should be noted that narrow peaks should be supported by a detector (e.g., MS/MS) with a fast scan speed or cycle time (or loop time) because it requires sufficient data points across the peak width for reliable and repeatable chromatographic data. The GC-MS/MS instruments recently released are known to be capable of producing consistent chromatographic data by rapidly providing sufficient points for narrow peaks while maintaining quantitative accuracy.

Figure 3. A schematic diagram of the GC-MS/MS.


Auto injector
Syringe
Inlet
Transfer line
Column
Q1
Ar
Q3
Detector
Ion source
Q2
(Collision cell)
Electron
multiplier
Vacuum state
Pump

Liquid chromatography-triple quadrupole mass spectrometry

Compared with GC, LC methods to analyze pesticide residues were applied more rarely in the past, because traditional ultra violet detector (UVD) and fluorescence detectors (FLD) usually have less selective and sensitive. Recently, MS (quadrupole, ion trap, or time-flight mass analyzers) equipped with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) have become widely regarded as the preferred techniques for the qualification and quantification.

For GC analysis, the target compounds must be volatile and thermally stable, but LC can analyze the non-polar compounds as well as thermally labile pesticides. Actually, the high number of pesticides belong to carbamates, urea herbicides, benzoylurea insecticides, and benzimidazole fungicides are known to more amenable to LC (Sannino, 2008). In addition, the need to analyze the more polar pesticides (e.g., glyphosate, glufosinate, and 2, 4-D) is one of the main reasons for frequent use of LC-MS/MS than GC-MS or GC-MS/MS. The wide scope of pesticides covered and simple sample preparation is the main reason why LC-MS/MS is more frequently used for the detection, identification, and quantification of pesticides in food nowaday (Stachniuk and Fornal, 2016).

LC-MS/MS has become the first choice for detecting trace level of pesticide residue in recent with the availability of various LC separation techniques including reverse phase, normal phase, hydrophilic interaction liquid chromatography, and/or ion chromatography. Also, many kinds of analytical columns having different column length, inner diameter, particle size, types of absorbents can accelerate the applicability of LC-MS/MS. Besides column, the capability of modifying the mobile phase and various flow rate and pressure like ultra-pressure liquid chromatography (UPLC) can be contribute to the usability.

In GC-MS ionization technique, the disadvantage of electron ionization (EI) is a strong ionization procedure. In many case, the molecular ion formation is not available due to extensive fragmentation (-70 eV). Thus, the most valuable information of the molecular weight of the unknown compound is difficult to obtain, In this case, the structure can be determined only by using the ion fragment pattern (Konstantinou, 2015).

However, LC-MS/MS equipped with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI), which gives a more soft ionization and selective fragmentation, is more useful to understand the molecular weight as well as most common MS analyzers. Because of the characteristic soft ionization, the ionized molecular ion could survive in ionization process, while the EI, which is type of strong ionization, most of the molecular ion is broken down owing to high electron energy.

In addition, it can be applied for highly polar, volatile, or thermally unstable compounds. The ESI and older but improved APCI are the most commonly used ionization techniques throughout the world in LC-MS applications for pesticides. The schematics of ESI source and APCI source are present in **Figure 4.** It is confusable, both techniques are basically belongs to atmospheric pressure ionization (API) techniques. As the name suggests, API firstly ionizes analyte under atmospheric pressure conditions, which makes it especially useful for removing solvents outside a vacuum, then mechanically and electrostatically separated from neutral molecules. The follows explanations were from the information of instrument by manufacturer Shimadzu (Introduction to LC-MS, 2017). ESI generates ionized ions in solution state before it reaches the mass spectrometer. Next, the ESI pulls sample solutions to the tip of a capillary tube adding a high voltage of about 3 to 5 kV. A nebulizer gas (nitrogen) surrounds the capillary tube to spray the

sample. This makes a fine mist of charged droplets with the same polarity as the applied voltage. While these charged particles are moving, the solvents continue to evaporate, thereby increasing the electric field on the decreased droplet surface. When the mutual repulsive force of the charges exceeds the liquid surface tension, then fission occurs. It is thought that as this evaporation and fission cycle is repeated, the droplets eventually become small enough that the sample ions are released into the gas phase (Introduction to LC-MS, 2017).

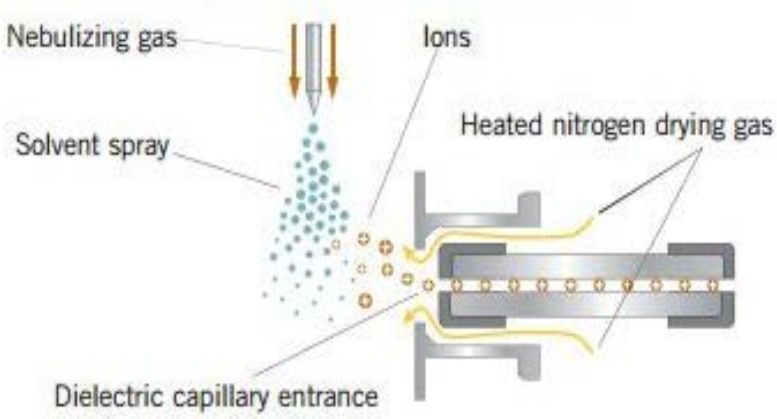
The other ionization method is APCI, which is a type of chemical ionization, just like CI for GC-MS. Although the ion source design is similar to ESI, the ionization principle is quite different. APCI vaporizes solvent and sample molecules by spraying the sample solution into a heater (400 °C) using a gas (N_2). Solvent molecules are ionized by corona needle to generate stable reaction ions. The protons are transferred between these reaction ions and sample molecules to ionize sample molecules by either adding (+e) or removing a proton (-e). These ion-molecule reactions are known to involve several patterns, such as proton-transfer reactions and electrophilic addition reactions (Introduction to LC-MS, 2017). Because ESI ionize the molecule using solution of mobile phase as described above, the mobile phase selection can affect peak response, and is an important consideration during method development (Particle-Sciences, 2009).

The analysis of residues in trace levels has been a great challenge in terms of reliability of data for regulatory compliance. LC-MS/MS along with GC-MS/MS has become the main choice for conducting trace level determination of pesticide residue in fruits and vegetables. Even though its prices are not cheap, when the think about alternative benefits, it is valuable and not so much expensive. Because these techniques give many revolutionary

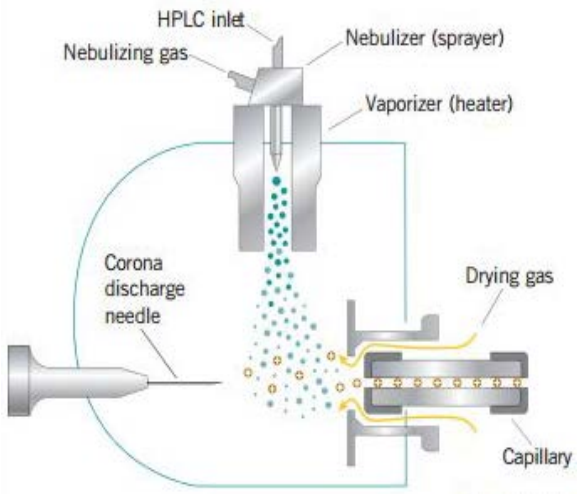
advantages including simultaneous determination, high sensitivity and selectivity, and time-saving with simple sample preparation.

Figure 4. Schematics of (A) electrospray ionization (ESI) and (B) atmospheric pressure chemical ionization (APCI) sources (Particle-Sciences, 2009) .

(A) ESI ionization



(B) APCI ionization



Definitions of terms relating to mass spectrometry

While new technology deal with mass spectrometry being released in every year, new terminologies also has been produced by many researchers. Sometimes we face to trouble in communication at the meeting with other researcher or reading a published paper. The use of inaccurate terminology could make an error in communication. To avoid confusing in using the terminologies, the frequently used terminologies in mass spectrometry are summarized based on the document from IUPAC Recommendations in 2013 (Murray Kermit et al., 2013).

- **Exact mass**; *"Calculated mass of an ion or molecule with specified isotopic composition."* The exact mass of an isotopic species (more appropriately, the calculated exact mass) is obtained by summing the masses of the individual isotopes of the molecule. For example, the exact mass of water containing two hydrogen (^{1}H) and one oxygen (^{16}O) is 1.0078 + 1.0078 + 15.9949 = 18.0105. When an exact mass value is given without specifying an isotopic species, it normally refers to the most abundant isotopic species.

- **Accurate mass** *"Experimentally determined mass of an ion of known charge"* It can be used to determine elemental composition to within limits defined by both the accuracy and precision of the measurement. Accurate mass and exact mass are not synonymous.

- **Nominal mass:** *"Mass of a molecular ion or molecule calculated using the isotope mass of the most abundant constituent element isotope of each element rounded to the nearest integer value and multiplied by the number of atoms of*

each element." For example, H = 1, C = 12, O = 16, etc. The nominal mass of H_2O is 18.

- Monoisotopic mass: *"Exact mass of an ion or molecule calculated using the mass of the most abundant isotope of each element."* For example, hydrogen (H) is 1.007825, carbon (C) is 12.00000, and oxygen (O) is 15.99491. For typical organic compounds, where the monoisotopic mass is most commonly used, this also results in the lightest isotope being selected.

- Average mass: *"Mass of an ion or molecule weighted for its isotopic composition."*

- GC-MS? or GC/MS? (hyphenate or slash ?);

The hyphen (-), or alternatively the slash (/, forward stroke), can be used to indicate combined methods such as gas chromatography separation combined with mass spectrometry detection. Gas chromatography-mass spectrometry or alternatively as gas chromatography/mass spectrometry (The corresponding abbreviations are GC-MS or GC/MS). First use to express the combination of separation methods are the *hyphen* in 1960s, next is the *slash* in 1970s, and "*hyphenated techniques*" in 1980s. Prefer expression is differ from journal. "Rapid Communications in Mass Spectrometry" and "Journal of Chromatography" are the slash (/) recommend whereas IUPAC recommend the hyphen (-). Currently, hyphens and slashes are used interchangeably.

- Precursor ion or Progenitor ion: *"Ion that reacts to form particular product ions or undergoes specified neutral losses."* The "Parent ion" terminology is deprecated. The reaction can be of different types including unimolecular

dissociation, ion/molecule reaction, change in charge state, possibly preceded by isomerization.

- **Product ion:** *"Ion formed as the product of a reaction involving a particular precursor ion."* The "Daughter ion" terminology is deprecated.

- **Selected reaction monitoring (SRM):** *"Data acquired from one or more specific product ions corresponding to m/z selected precursor ions recorded via two or more stages of mass spectrometry."*

- **Multiple reaction monitoring (MRM):** *"Application of selected reaction monitoring to multiple product ions from one or more precursor ions."* This term should not be confused with consecutive reaction monitoring, which involves the serial application of three or more stages of selected reaction monitoring.

- ***m*/*z*:** Abbreviation representing the dimensionless quantity formed by dividing the ratio of the mass of an ion to the unified atomic mass unit, by its charge number (regardless of sign). The abbreviation is written in italicized lowercase letters with no spaces. Mass-to-charge ratio has been used occasionally for the horizontal axis in a plot of a mass spectrum, although the quantity measured is not the ion's mass divided by its electric charge (SI units kg $C^{-1)}$. However, *m/z* is recommended as an abbreviation to represent the dimensionless quantity that is used almost universally as the independent variable in a mass spectrum. The "Mass-to-charge ratio" and the "*thomson* (*Th*) unit" are deprecated.

- Electron ionization (EI): Ionization that removes one or more electrons from an atom or molecule through interactions with electrons that are typically accelerated to energies between 10 and 150 eV. The “electron impact ionization” is deprecated.

- Electrospray ionization (ESI): Spray ionization process in which either cations or anions in solution are transferred to the gas phase via formation and desolvation at atmospheric pressure of a stream of highly charged droplets that result from applying a potential difference between the tip of the electrospray needle containing the solution and a counter electrode. (electro-spray, false expression)

- Collision-induced dissociation (CID) = collisionally activated dissociation: ***“****Dissociation of an ion after collisional excitation.”*

- Centroid acquisition: Procedure of recording mass spectra in which an automated computer-based system detects peaks, calculates the centroid based on the average m/z value weighted by the intensity, and assigns m/z values based on a calibration file. Only the centroid m/z value and the peak magnitude are stored.

- Profile mode: Method for acquiring a mass spectrum where each peak is displayed as a curve, with the data points defining the curve corresponding to the signal intensities at each particular *m/z* value.

- Linearity of calibration curve, R^2? or r^2?: Coefficient of determination, pronounced "R squared". It indicates the proportion of the variance in the

dependent variable that is predictable from the independent variable. The r^2:is used for a simple linear regression whereas the R^2 is used in for coefficient of multiple correlation (Coefficient_of_determination, 2017). Therefore, in pesticide quantitation, the coefficient of calibration curves expressed by the "r^2" may be more proper because simple linear regression which is consist of area (height) and response has been used.

Trends in sample preparation method

Covering the wide scope of pesticides with simple sample preparation has been always challenges in pesticides multiresidue analysis. In recent years, many kinds of methods has been introduced to the development of new sample preparation method, which can save analysis time, labor, cost and environmental friendly. All of the methods has goals of improving the analytical performance of the procedure. This paragraph present the representative methods, has been widely used for pesticides multeresidue.

As the concern for food safety is increased, it has become an important issue to determining the residual pesticides accurately in the food. However, the complicated matrix of agricultural produce may affect the accuracy of the analysis (Liu, Liu, et al., 2016). The innovation of MS has revolutionized the extraction step for pesticide residue determination because it has great selectivity and sensitivity (Caldas et al., 2011).

For multiresidue sample preparation combined with the MS or MS/MS techniques, the QuEChERS (quick, easy, cheap, effective, rugged, and safe) method has widely replaced the traditional sample treatment methods such as column chromatography or solid phase extraction (SPE) since it was first introduced by Anastassiades and co-workers in 2003 (Anastassiades, Lehotay, et al., 2003; Anastassiades, Maštovská, et al., 2003). Especially, dispersive SPE (dSPE) cleanup is simple but offers high accuracy and precision (Alder et al., 2006; Chamkasem et al., 2013; Wong et al., 2010). The dSPE typically uses primary-secondary amine (PSA) sorbent for removal of some organic acids, sugars, and fatty acid (Anastassiades, Lehotay, et al., 2003; Lehotay, Maštovská, et al., 2005). Optional sorbents such as graphitized carbon black (GCB)(Li et al., 2009; Wong et al., 2010) and ChloroFiltr (Walorczyk et al., 2015a) can be applied with PSA to remove pigment such as chlorophyll or carotenoid.

Recently, multiwalled carbon nanotubes (MWCNT) were also introduced as cosorbents for reduction of matrix interferences (Han et al., 2017; Zou et al., 2016).

Currently, the combination of QuEChERS and the MS/MS technique is one of the most popular analytical approaches for the multiresidue analysis in various food matrices (**Table 1**) (Cho et al., 2016; He, Chen, et al., 2015; He, Wang, et al., 2015).

Table 1. Overview of published studies in recent three years for the analysis of pesticides multiresidue using QuEChERS methodology.

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Oolong tea	89	GC-MS/MS	QuEChERS	(Wu, 2017)
Shallot, ginger, garlic, onion, leek and celery	38	GC–MS	Column chromatography	(Wang et al., 2017)
Tomato, apple, leek and orange	210	GC-High resolution(HR) MS	Citrate QuEChERS	(Uclés et al., 2017)
Black currants, red currants, raspberries, cherries, strawberries, blackberries, cauliflowers and broccoli	60	LC-MS/MS	QuEChERS	(Stachniuk et al., 2017)
Lettuce	16	LC-MS/MS	Modified QuEChERS	(Ribeiro Begnini Konatu et al., 2017)

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Atlantic salmon feeds	156	LC-QTOF	QuEChERS	(Regueiro et al., 2017)
Baby food	16 (pyrethrins and pyrethroids)	LC-MS/MS	salting-out assisted liquid–liquid extraction	(Petrarca et al., 2017)
Globe artichoke leaves and fruits	35 GC and 63 LC	GC-MS and LC–MS/MS	Modified QuEChERS	(Machado et al., 2017)
Rice	58	LC–MS/MS	Modified QuEChERS	(Liu et al., 2017a)
Fish samples	10	LC–MS/MS	SPE cleanup	(Liu et al., 2017b)
Honeybees	84	LC-MS/MS and GC-MS/MS	QuEChERS	(Kiljanek et al., 2017)
Fatty fish and liver matrix	340	LC–MS/MS	Modified QuEChERS	(Kaczyński et al., 2017)
Oilseed samples	120	LC–MS/MS	Modified QuEChERS	(Kaczyński, 2017)
Onion, wheat, potato and pea	11	LC–MS/MS	modified QuPPe (Quick Polar Pesticides) protocols	(Kaczynski, 2017)

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Rice, wheat, and corn	124	GC-MS/MS	Modified QuEChERS	(Han et al., 2017)
Honeybee wax	160	GC-MS/MS	Modified QuEChERS	(García et al., 2017)
Leek	183	GC-MS/MS	Modified QuEChERS	(Zou et al., 2016)
Straw Roughage	69	LC–MS/MS	Modified QuEChERS	(Zhang et al., 2016)
Honey	200	GC–MS/MS	Modified QuEChERS	(Shendy et al., 2016)
Orange juice	74	LC–MS/MS	Modified QuEChERS	(Rizzetti et al., 2016)
Apple, Citrus fruits, peanut, spinach, leek, green tea	25	LC–MS/MS	Modified QuEChERS , Multi-plug filtration cleanup (m-PFC)	(Qin et al., 2016)
Sugar beet and beet molasses	400	GC-MS/MS and LC–MS/MS	Modified QuEChERS, matrix solid phase dispersion (MSPD)	(Lozowicka et al., 2016)
Lettuce and orange	175	GC-MS/MS and LC–MS/MS	Dutch mini-Luke extraction method	(Lozano, Kiedrowska, Scholten, de Kroon, de Kok and Fernandez-Alba, 2016)

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Olive oil, olives and avocado	67	LC–MS/MS	Modified QuEChERS, Enhanced Matrix Removal-Lipid (EMR)	(López-Blanco et al., 2016)
Chinese material medica	74	GC-MS/MS	Acetate buffered QuEChERS	(Liu, Li, et al., 2016)
Green tea leaves	101	GC–MS/MS	Modified QuEChERS	(Hou et al., 2016)
Cowpea	171	GC–MS/MS	Modified QuEChERS, Multi-walled carbon nanotubes (MWCNTs)	(Han, Song, et al., 2016)
Rice and Wheat Flour	100	GC–MS/MS	Modified QuEChERS	(Grande-Martínez et al., 2016)
Edible oils (olive, soya and sunflower)	165	LC–MS/MS	Modified QuEChERS, EMR	(Dias et al., 2016)
Brown rice, red pepper and mandarin orange	113	GC–MS/MS	EN QuEChERS	(Cho et al., 2016)
Green tea, ginseng, gingko leaves, saw palmetto, spearmint, and black pepper	227	GC–MS/MS	Modified QuEChERS	(Chen et al., 2016)

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Avocado, orange, spinach, honey, and hazelnut	381	LC–HRMS	Modified QuEChERS	(Yang et al., 2015)
Green soybean	100	GC–MS/MS	Modified QuEChERS with Z-Sep	(Walorczyk et al., 2015b)
Lupin, white mustard and sorghum	100	GC-MS/MS and LC–MS/MS	Modified QuEChERS, ChloroFiltr	(Walorczyk et al., 2015a)
Tomatoes	109	LC–MS/MS	Modified QuEChERS	(Golge and Kabak, 2015)
The vegetable and fruit samples	60	UHPLC/TOF–MS	SPE cartridge (PSA)	(Sivaperumal et al., 2015)
tomato, red pepper, sour cherry, dried apples, black currant powder, raisins, wheat flour, rolled oats, and wheat germ.	120	GC–MS/MS	Modified QuEChERS	(Rasche et al., 2015)
Pollen	253	LC–MS/MS	Modified QuEChERS	(Vazquez et al., 2015)
Soya-based nutraceutical products	177	GC–MS/MS	Modified QuEChERS	(Palenikova et al., 2015)

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Dietary supplements from grape seed extracts	130	GC–MS/MS	Modified QuEChERS	(Nieto-García et al., 2015)
Chinese medicines	107	GC-NCI-MS/MS	Modified QuEChERS	(Nie, Miao, et al., 2015)
green tea	100	LC–MS/MS	Modified QuEChERS	(Martínez-Domínguez et al., 2015)
Grape, mango, drumstick, bitter gourd, capsicum, curry leaf, and okra	296	LC–MS/MS	buffered ethyl acetate extraction method	(Jadhav et al., 2015)
Salmon	185	GC–MS/MS	Modified QuEChERS	(Holmes et al., 2015)
Leek and garlic	213	GC–MS/MS	Modified QuEChERS	(He, Chen, et al., 2015)
Black, green, oolong, and white Teas	227	GC–MS/MS	Modified QuEChERS	(Hayward et al., 2015)
Tobacco	259	GC–MS/MS	Modified QuEChERS	(Khan et al., 2015)

Matrix	No. of pesticides	Instrument	Sample preparation	Reference
Tomato	57	LC–MS/MS	Modified QuEChERS	(Andrade et al., 2015)
Chinese cabbage and cucumber	238	LC–MS/MS	Modified QuEChERS	(Zhao, Feng, et al., 2014)
Tomato and tomato products	186	GC–MS/MS	Column chromarography, m-PFC	(Zhao, Huang, et al., 2014)
tomato, potato, spring onion and orange	210	GC–MS/MS	Modified QuEChERS	(Ucles et al., 2014)
Cucumber and tomato	101		Modified QuEChERS, MNPs	(Li et al., 2014)

GC-MS/MS and LC-MS/MS can generally play a complimentary role for each other because some unique compounds are only amenable to one of the techniques. A wide range of multi-residual analysis using LC-MS/MS has been carried out, but with GC-MS/MS not many studies on multi-residual analysis (over 300 pesticides) were not performed (Chamkasem et al., 2013; Cho et al., 2016; He, Chen, et al., 2015; He, Wang, et al., 2015; Holmes et al., 2015) while 541 pesticides were reported to be GC amenable on GC-MS by Pang et al. (2009). Recent study on multiresidues in botanical samples identified 310 pesticides with GC-MS/MS but considered each isomer peak as an individual compound (Hayward et al., 2013). In addition, not many studies have focused on the optimization of GC-MS/MS to increase the number of the GC amenable pesticides. Therefore, several GC and MS/MS conditions (e.g. column, selection of precursor and product ions) still need to be optimized for maximization of the number of GC amenable pesticides without compromising sensitivity and selectivity. (Cho et al., 2016)

QuEChERS methodology

The QuEChERS methods is most widely used method in recently, has been readily accepted as “golden standard” in multiresidue analysis. Nowadays, the more than the half of the published papers has been cited the QuEChERS method, and most of them used QuEChERS method or the modified methods. The name of the QuEChERS is an acronym word from "Quick, Easy, Cheap, Effective, Rugged, and Safe” that explains perfectly all the advantages of this method. A single step acetonitrile extraction and salting out by liquid–liquid partitioning to remove residual water in the sample with $MgSO_4$ followed by a dispersive solid-phase extraction (dSPE) clean-up is a key process. (Walorczyk, 2008). This approach can allow plenty of samples in a short time and extract a large number of pesticides with satisfactory efficiencies.

It was developed by Michelangelo Anastassiades in the years 2001 and 2002 during his post-doctoral visit at the USDA , Pennsylvania (USA) in the research group of Steven Lehotay (http://quechers.cvua-stuttgart.de, 2011). The original method was presented in June 2002 at the European Pesticide Residue Workshop (EPRW), in the following year, the detailed method was firstly published in 2003 (Anastassiades, Lehotay, et al., 2003). To improve the recoveries of pH-dependent analytes, the original method was modified in 2004 by Lehotay, Maštovská, et al. (2005). In this study, they employed the acetate buffering to achieve a pH value of 6 for all samples. This modification have been adopted as the Association of Analytical Communities (AOAC) Official Method (Lehotay, 2007). In 2008, the Anastassiades modified again the method to citrate buffered methods, resulted in the European Standard EN 15662 (2008).

Table 2 summarized the details of the representative QuEChERS methods. The original QuEChERS method was developed to allow the extraction of pesticide residues in fruits and vegetables having high ratio of water. Later, the original unbuffered method have been modified to AOAC methods in order to stabilization of acidic pesticides and protection of base-sensitive pesticides. The pH value in extraction procedure is approximately 4.8 due to strong acetate buffering. The citrate buffered method (EN 15662) was also introduced to adjust the pH in the first extraction/partitioning step to a compromise value of 5 to 5.5. In this range, most of the pesticides having the characteristics of acidic or alkaline-labile are sufficiently stabilized.

The one of the most innovative technology in QuEChERS methodology is the dSPE, which is easy and simple cleanup procedure. A sample extract is added to a centrifuge tube containing a relatively small amount of sorbent (e.g. PSA, C18, GCB) and the tube is shaken to increase distribute the SPE material and facilitate the clean-up process. Next, the separation of the sorbent is capable by centrifugation of the sample and the supernatant can be analyzed. The undesirable co-extracted compounds from the matrix are adsorbed to sorbents, the analytes of interest allow to remain in the liquid phase (Rejczak and Tuzimski, 2015).

Dispersive SPE has several advantages against classical solid phase extraction : (1) no need of SPE manifold and vacuum/pressure, (2) no conditioning step needed, (3) no problems with channeling, flow control, and drying-out, (4) no need to elute, (5) no evaporation needed, (6) No need of additional vessel for eluent collection, (7) less sorbent needed, (8) faster and cheaper, and (9) no experience to perform needed (Anastassiades, 2006).

Table 2. The representative QuEChERS methods.

	Original QuEChERS	Acetate buffered QuEChERS (AOAC)	Citrated buffered QuEChERS (EN 15662)
Developed year	2003	2007	2008
Sample (g)	10 g	15 g	10 g
Extraction solvent	10 mL of Acetonitrile	15 mL of acetonitrile with 1% acetic acid	10 mL of Acetonitrile
Partitioning reagent	4 g of $MgSO_4$, 1 g of NaCl	6 g of $MgSO_4$, 1.5 g of NaOAc	4 g of $MgSO_4$, 1 g of NaCl, 1 g of $Na3Cit.2H_2O$, 0.5 g of $Na2Cit.25H_2O$
Cleanup (dispersive SPE)	150 mg of $MgSO_4$, 25 mg of PSA	150 mg of $MgSO_4$[a], 50 mg of PSA	150 mg of $MgSO_4$, 25 mg of PSA
Option (additional absorbents)			
Fatty sample	-	+50 mg of PSA	+50 mg of PSA
Pigment sample	-	+50 mg of GCB	+2.5 mg of GCB or +7.5 mg of PSA

-$MgSO_4$: magnesium sulfate, NaCl: sodium chloride, NaOAc: sodium sulfate, $Na3Cit.2H_2O$: disodium hydrogencitrate sesquihydrate, $Na2Cit.25H_2O$: trisodium citrate dehydrate, PSA: primary-secondary amine, GCB: graphite carbon black

PSA absorbent is the key element in cleanup procedure. PSA is a weak anion exchanger that can remove sugars, fatty acids, polar organic acids, and some pigments, and some sugars (Koesukwiwat et al., 2008; Walorczyk and Gnusowski, 2009). Because the polar and acidic pesticides could retained by PSA, the EN 15662 suggested that acidic pesticides should be directly analysed from the raw extract without PSA clean-up. But the PSA have not much effect on removal of the color from chlorophyll and carotenes (Lehotay, Maštovská, et al., 2005).

Anhydrous magnesium sulfate ($MgSO_4$) can act a moisture absorbent, removing residual water remaining in an organic phase. It should be noticed that when the $MgSO_4$ absorb the water, much of the heat is produced in partitioning step. The produced heat can caused decomposition of thermally label pesticides. According to the particle size, there is a difference in types of heat release in my experience. In the case of powdered type $MgSO_4$, strong heat is released initially, while the semi-granule types of $MgSO_4$ generate the heat gradually. Geis-Asteggiante et al. (2012) reported that the use of an ice bath for reducing the temperature during the extraction had no significant effect on recoveries of captan, captafol, and folpet, probably due to inherent analytical difficulties more than temperature. However, it should be careful that in the case of the sample having high moisture contents, the centrifuge tube can explode or be broken by increased inner volume by high temperature in our experience. The temporarily storage in ice bath or dry ice prior to adding the $MgSO_4$ can be useful to decrease the temperature in the extraction tube.

Additional absorbent can be applied with PSA and $MgSO_4$ in cleanup step. The graphite carbon black (GCB) removes chlorophyll and pigments from the extracts in dispersive SPE, but it is well known that planar pesticides can

also strongly retains by GCB (Lehotay, Mastovska, et al., 2005) (Li et al., 2009). According to visible green color, the different amounts (2.5 and 7.5 mg) of GCB can be applied (EN 15662). The excessive addition of GCB in dSPE procedure cause the losses of planar of aromatic pesticides such as thiabendazole, hexachlorobenzene, and pentachlorobenzene (Walorczyk, 2008; Wong et al., 2010). Mol et al. (2007) have reported that the addition of toluene solvent which is planar solvent in cleanup step increased the recoveries of planar pesticides while the co-extracts was also increased. Although other sorbents such as CarbonX and ChloroFiltr has been also introduced, the similar phenomenon showing unacceptable recoveries in certain analytes was observed as more chlorophyll is removed (Han, Matarrita, et al., 2016; Morris and Schriner, 2015; Walorczyk et al., 2015b). The multi-walled carbon nanotubes (MWCNTs) also are a relatively new type of nanotube material that was reported to be a good sorbent for the purpose of removal of chlorophylls and pigments in vegetables and teas (Guan et al., 2011; Han et al., 2017; Ravelo-Pérez et al., 2008; Zhang et al., 2016; Zhao et al., 2012)

The use of C18 (octadecylsilyl-derivatized silica)) also can eliminate long-chain fatty compounds, sterols, and other nonpolar interferences like a lipid. Co-extracted lipids in the extracts can be eliminate to a high degree by a freezing-out step or a C18 clean-up (EN 15662). The other sorbents such as Z-Sep and Z-Sep Plus also can be applied to remove for the lipid. These alternatives products are commercially available are offered by Supelco. The Z-Sep is a sorbent based on modified silica gel with zirconium oxide and the Z-Sep Plus sorbent consists of both zirconia and C18 dual bonded on the same silica particles. These innovative dispersive phases demonstrate ability to extract more fat and pigment than conventional PSA and C18 sorbents and

show greater recovery with better reproducibility (Kiljanek et al., 2016; Li et al., 2015; Lozano et al., 2014; Rajski et al., 2013). Other novel commercially available sorbents is EMR-Lipid (Enhanced Matrix Removal of Lipids) from Agilent. The structure of EMR-Lipid is not well known, and it does not function as a solid adsorbent in dSPE, but it dissolves to saturation in extract solution, and its mechanism is known to involve both size exclusion and hydrophobic interactions (Han, Matarrita, et al., 2016). The manufacturer claims that EMR-Lipid selectively removes lipids from QuEChERS extracts of fatty foods (Kaczynski et al., 2017) (Han, Matarrita, et al., 2016)

In the case of the dry commodities such as cereals, dried fruits or tea require the presoaking of samples by addition of water prior to extraction in order to weaken interactions of pesticides with the matrix. As seen **Table 3**, the EN 15662 standards suggested that different volume of water as well as sample weight should be added according to commodities in order to compensate the moisture contents (2008).

Table 3. The EN 15662 method guidelines for the addition of water into commodities with low water content.

Commodities	Sample weight	Water addition	Note
Fruits and vegetables with water content over 80%	10 g	-	-
Fruits and vegetables with 25–80% water content	10 g	X g	X = 10 g – water content in 10 g sample
Cereals	5 g	10 g	-
Dried fruits	5 g	7.5 g	Water can be added during homogenization step
Honey	5 g	10 g	-
Species	5 g	10 g	-

Validation of analytical method

Analytical method must be prove to be secure the reliability of results so that the data can have confidence from test client. For these reasons, method validation and verification are essential requirements of accreditation to ISO/IEC 17025 and ISO 15189 (NATA, 2012). Through the validation procedure, new or modified methods get recognition in its suitableness for its intended purpose. The quality, reliability, and consistency of analytical results could be judged by the results from method validation. Therefore, analytical methods need to be validated, verified, or revalidated in the following instances (Huber, 2010); in the case of the initial use in routine analysis, a transferring a method to another laboratory, and whenever the conditions or method parameters for which the method has been validated change and the change is outside the original scope of the method. In this paragraph, various validation parameters are summarized and compared on the basis of comprehensive international and national guidelines on the requirements of analytical methods and validation protocols.

Accuracy/Trueness

International Conference for Harmonization (ICH) defines the accuracy of an analytical procedure expresses the closeness of agreement between the value which is accepted either as a conventional true value or an accepted reference value and the value found. It is usually determined (average of a replicated set of trials) by recovery test. Recovery is defined as the amount measured as a percentage of the amount of analyte(s) (active substance and relevant metabolites) originally added to a sample of the appropriate matrix, which contains either no detectable level of the analyte or a known detectable level. Recovery experiments provide information on both precision and trueness (bias), and thereby the accuracy of the method (OECD, 2007). The use of certified reference materials or reference method of known uncertainty can be also used for estimate the accuracy. The method of fortification of spiked samples should be described (Fong 1999).

Precision/ Repeatability/Reproducibility

Precision is defined as the closeness of agreement between independent test results obtained under stipulated (predetermined) conditions. The measure of precision usually is expressed in terms of imprecision and computed as standard deviation of the test result. Less precision is determined by a larger standard deviation (Bratinova et al., 2009). There is two kinds of terms expressing the precision (repeatability and reproducibility). The repeatability defined as the closeness of agreement between mutually independent test results obtained with the same method on identical test material, in the same laboratory by the same operator using the same equipment within short intervals of time, while the reproducibility refers to the closeness of agreement between independent

results obtained with the same method on identical test material obtained but under different conditions (OECD, 2007; Unsworth, 2010). The different criteria to validate the accuracy/trueness and precision/repeatability is summarized in **Table 4**

Table 4. The criteria of accuracy or trueness in representative organizations. The criteria indicate range of mean recovery, % (relative standard deviation, %).

	CODEX[a] (CAC/GL 40-1993)	EU[b] (SANTE)
≤1 μg/kg	50-120 % (≤ 35%)	70-120 % (≤ 20%)
> 1 μg/kg ≤ 0.01 mg/kg	60-120 % (≤ 30%)	
> 0.01 mg/kg < 0.1 mg/kg	70-120 % (≤ 20%)	
> 0.1 mg/kg < 1.0 mg/kg	70-110 % (≤ 15%)	
> 1 mg/kg	70-110 % (≤ 10%)	
Note		A minimum of 5 replicates is required at LOQ and at least one other levels

[a] Guidelines on good laboratory practice in pesticide residue analysis (Codex 2003),

[b] Guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed (European Commission, 2015).

Detection limit/Limit of quantitation (LOQ)/ Limit of quantitation (LOD)

The different definitions is being used in the terms of detection limit/Limit of quantitation (LOQ)/ Limit of quantitation (LOD). According to the several guideline, concepts are presented as follows.

1) EU (SANTE guideline)(European Commission, 2015)

- LOD: The terms of the LOD is not explicitly defined, while the LOQ is defined as the minimum concentration or mass of the analyte that can be quantified with acceptable accuracy and precision. It should be apply to the complete analytical method. The LOQ can be set by lowest spike level meeting the method performance criteria for trueness and precision (mean recovery 70-120% with ≤ 20% of RSD). Also, the LOQ should be lower than those maximum residue limit (MRL).

2) CODEX(Codex 2003)

- LOD: smallest concentration where the analyte can be identified. Commonly defined as the minimum concentration of analyte in the test sample that can be measured with a stated probability that the analyte is present at a concentration above that in the blank sample.
- LOQ: Smallest concentration of the analyte that can be quantified is also called to LOQ. The LOQ is commonly defined as the minimum concentration of analyte in the test sample that can be determined with acceptable precision (repeatability) and accuracy under the stated conditions of the test.

3) OECD guideline (OECD, 2007)

- LOD: the lowest amount of an analyte in a sample that can be detected but not necessarily quantitated as an exact value. At the limit of detection, a positive identification can be achieved with reasonable and/or previously determined confidence in a defined matrix using a specific analytical method. The LOD is typically not required. However, if needed for a refined

assessment (or some other purpose), an explanation of how the LOD was derived should be provided.

- LOQ: defined from a regulatory perspective as the lowest concentration tested at which an unambiguous identification of the analyte can be proven and at which an acceptable mean recovery with an acceptable relative standard deviation (RSD) is obtained, also referred to as the LOD or Lowest Limit of Method Validation (LLMV). The LOQ should be low enough to achieve the intended purpose of the method. From an analytical perspective, 6-10 times the standard deviation of the noise provides an estimate of the LOQ, which is then verified by the fortification experiments.

Calibration curve and linearity

Calibration refer to the capacity of detection to produce an acceptable correlation between the instrumental response and the quantity of the analyte in the sample. There was no strictly criteria on linearity in general. But, most of guideline insisted that the analyte concentration to be measured should be within the defined dynamic range of the instrument (Unsworth, 2010). The representative criteria on calibration is presented as follows:

1) EU (SANTE guideline)(European Commission, 2015)

-The lowest calibration level (LCL) must be equal to, or lower than, the calibration level corresponding to the reporting limit (RL). The RL must not be lower than the LOQ. Multi-level calibration is preferred. The use of weighted linear regression (1/X) is recommended, rather than linear regression.

2) CODEX (Codex 2003)

- For linear calibration: regression coefficient for analytical standard solutions (r) $\geq$ 0.99, the SD of residuals (Sy/x) $\leq$ 0.1 3). In the case of

screening method, for linear calibration, the regression coefficient should be (r) ≥ 0.98, SD of residuals ≤ 0.2. For polynomial function (r) ≥ 0.95

3) OECD guideline (OECD, 2007)

- Calibration refers to the ability of a detection system to produce an acceptable, well defined, correlation between the instrumental response and the concentration of the analyte in the sample. The analyte concentration to be measured should be within the defined dynamic range of the instrument.

The analytical calibration should extend over a range appropriate to the lowest and highest nominal concentration of the analyte in relevant analytical solutions. Either duplicate determinations at three or more concentrations or single determinations at five or more concentrations should be used.

Matrix effect

The high selectivity of MS/MS methods results in pure chromatograms without any noticeable interference in the form of extra chromatographic peaks or peak shoulders (Grujic et al., 2009). Although thanks to higher selectivity, it is possible to simplyfy the sample preparation procedure, some residues of matrix coextractives are extracted into the extraction solvent, the co-extracts from matrix components may interfere with peak response. The phenomenon which is higher peak response in matrix-environment than standard solution is regarded as signal enhancement, while the decreased peak response is regarded as signal suppression.

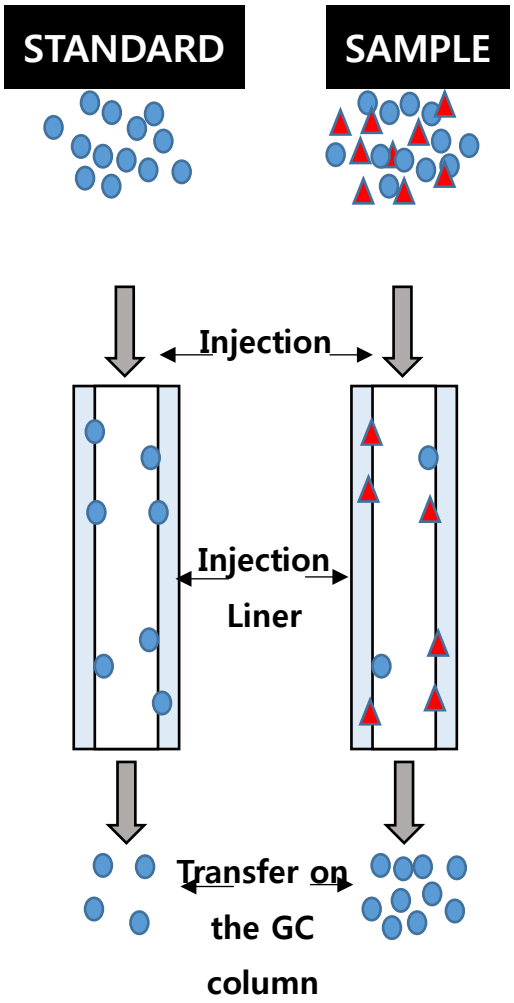
The term of “matrix effect” is defined as the direct or indirect alteration or interference in response due to the presence of unintended analytes (for analysis) or other interfering substances in the sample” (Shah et al., 2000). A general problem in GC analysis from matrix effect is the peak tailing and/or analyte losses due to undesired interactions with active sites in the inlet (liner, etc.) and column. Poor peak shapes or degraded peak response makes interfere to identify and quantify. In addition, it is generally observed that the response of target analyte coexisted with matrix components is higher than those from injected without matrix like pure solvent standard.

There are various different causes which can affect to matrix effect. Matrix effect in GC analysis usually expressed to matrix-induced chromatographic response enhancement. Significant peak quality improvements are observed for some analytes when they are injected in the presence of matrix since the matrix components cover the active sites with reduced analyte interactions. This phenomenon is regarded as “matrix-induced enhancement” (Erney et al., 1993).

Figure 5 illustrates the principle of matrix effect occurring in GC inlet. When standard solutions made by pure solvent analysed by GC, the analytes can bind to the active sites (e.g., free silanol groups or metal ions) presented in liner, injection port, glass wool, etc. and a smaller amount of target analytes are transferred to the analytical column and consequently detected (Zhao et al., 2012). But, when the target analytes are injected with matrix components, the co-extractives is contributed to occupy the active site, causing a larger amount of analyte is arrived at detector than when prepared in pure solvent. This phenomenon is used to explain recovery rates of pesticides that exceed 100% and the low accuracy of results (Hajšlová et al., 1998). Non-volatile matrix components, which can be easily accumulated in GC inlet, liner or front part of an analytical column by repeated injections, can give rise to successive formation of new active sites, which might cause another effect, sometimes called to matrix-induced diminishment. (Soboleva et al., 2000).

There can be several numbers of factors that can cause this to matrix-induced signal suppression or enhancement, which include (a) the number of active sites in the inlet and GC column, (b) chemical structure of the analytes, (c) concentration of analytes, (d) injection temperature, (e) interaction time (a function of flow rate, pressure, injection volume, solvent expansion volume, column diameter, and retention time), and of course (f) type and concentration of matrix (Banerjee and Utture, 2015).

Figure 5. Matrix effect in GC inlet.


STANDARD
SAMPLE
Injection
Injection
Liner
Transfer on
the GC
column

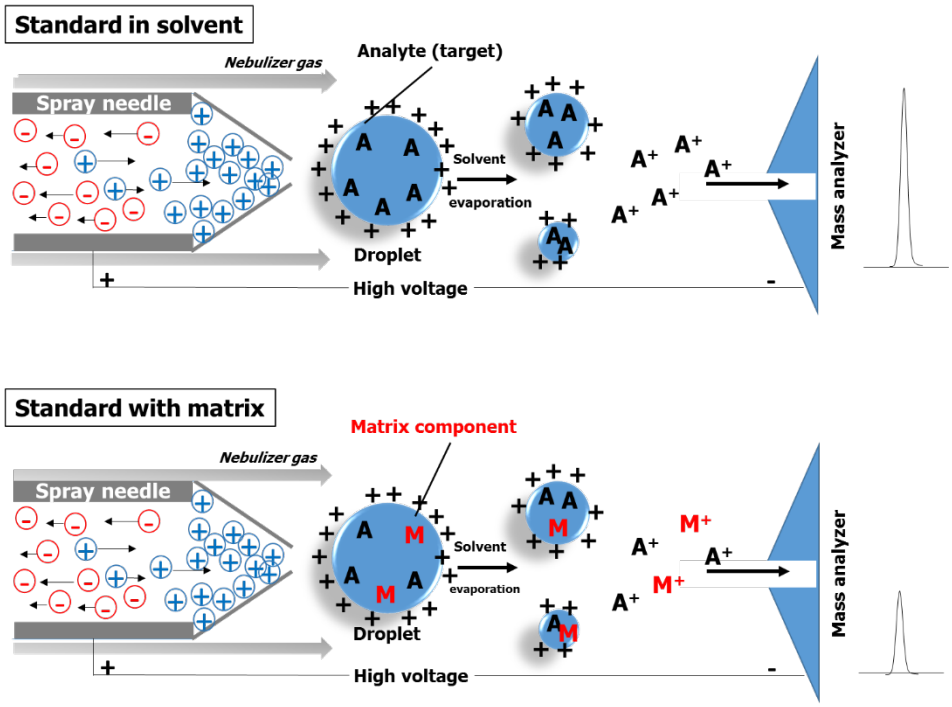
One of the most effective way to compensate the matrix effect is the use of matrix-matched standard and it is one officially accepted option in the EU for pesticide residue analysis in food and feed (EN15662, 2008). Most of the published paper use matrix matched calibration method. The making a matrix matched standards is very simple. It only requires blank extracts of the fortified sample. The matrix matched calibration is an external calibration using calibration standards prepared in matrix blank extract. However, in the case of routine pesticide residue analysis using many different sample types (e.g., different fruits and vegetables), the procedure of matrix matching is more difficult (Stahnke and Alder, 2015). In addition, the difficulty in obtaining residue-free control matrices which are exactly same with test sample still remains to challenges.

Another way to overcome matrix effect is the use of analyte protectants such as 3-ethoxy-1, 2-propanediol, D-sorbitol, shikimic acid, and ethylglycerol. The analyte protectant is capable to effectively block the active site in GC system. When the analyte protectant is added to both samples and standards, it can decrease the degradation and/or adsorption of target analytes by masking the active sites and consequently to minimize the matrix-induced enhancement effect (Maštovská et al., 2005; Rahman et al., 2013). However, the analyte protectant requires an additional preparation step (adding AP solution). Because many effective analyte protectants have usually polar and well-retained properties in the syringe of the injector and analytical column, specific management to prevent contamination or GC system by analyte protectant. As it mentioned in above, pesticide-free matrices or the exactly same matrix as the target sample is not always available for preparation of matrix-matched standards in routine analysis, analyte protectant can be useful to decrease the matrix effects.

In LC-MS or LC-MS/MS, detection of matrix effects is also troublesome problem and considered as factor for increasing an uncertainty of result. In the case of LC-MS, the matrix effects do not occur during chromatography process. Many researchers reported that the matrix effect may occur in ionization process by co-eluted with the analyte interfere in the MS detector (Chamkasem and Harmon, 2016; Chen et al., 2013; Matuszewski et al., 2003; Van Eeckhaut et al., 2009).

Different mechanisms have been introduced to explain the matrix effects in LC-MS. **Figure 6** present the major tentative mechanism of matrix effects (signal supression) in electrospray ionization (ESI). In ESI, analyte ionization efficiency is affected by matrix components with changed properties (e.g. viscosity) of the droplets (Bruins, 1998; King et al., 2000) (Kwon et al., 2012). A competition for a place on droplet's surface and competition for excess charge can be explain the signal suppression phenomenon in LC-MS/MS (Bruins, 1998). According to Bruins (1998)even in the high analyte concentrations of solvent standard, matrix effect may occur by attributing to the limited space on the surface of ESI droplets. Also with matrix components, the occupied the surface of the ESI droplet by co-eluting matrix components may decrease the chance of analytes to get ionized. For this reason, ion suppression effects tend to be more common and intense in the ESI. Unfortunately, this hypothesis is just tentative mechanism and the causes is not fully understood and still unknown. However, the competition for access to the droplet surface and for excess charges on the droplet surface seem to be the most important strong theory (Stahnke and Alder, 2015).

Figure 6. Factor for signal suppression in LC-MS/MS (ESI).


Standard in solvent
Nebulizer gas
Analyte (target)
Spray needle
Solvent
evaporation
Droplet
High voltage
Mass analyzer
Standard with matrix
Matrix component
Nebulizer gas
Spray needle
Solvent
evaporation
Droplet
High voltage
Mass analyzer

The purpose of the present study

This study aimed to develop an efficient and useful multiresidue screening method for the simultaneous analysis, which would include as many pesticides as possible in representative food commodities (brown rice, orange, spinach, and potato). GC-MS/MS and LC-MS/MS was used for analysis due to its advantages of both high sensitivity and selectivity for a wide range of target pesticides. Optimum multiple reaction monitoring parameters were optimized to cover the high number of pesticides. Furthermore, several practical manners including pulsed pressure injection, priming effect, function of automated adjustment of retention time (AART), injection volume in LC-MS/MS analysis to enhance sensitivity and usability were also evaluated. The QuEChERS (quick, easy, cheap, effective, rugged, and safe) approach to sample preparation has been demonstrated to serve the intended purpose for many pesticides in diverse sample types, were modified to more practical and efficient analysis without compromising these advantages or recoveries. In terms of limit of quantitation (LOQ), accuracy, and precision, the developed method was validated before it was finally applied for the screening of multiclass pesticides in real samples collected at Korean local markets.

Part 1

Rapid and Simultaneous Analysis of 360 Pesticides in Crops Using Microbore GC-MS/MS

The part of this part has been published as “Rapid and Simultaneous Analysis of 360 Pesticides in Brown Rice, Spinach, Orange, and Potato using Microbore GC-MS/MS”, ***Journal of Agricultural and Food Chemistry***, 2017, 65 (16), pp 3387–3395 and also “Sensitivity enhancement using a microbore column and pulsed pressure injection in the simultaneous analysis of 356 pesticide multiresidues by gas chromatography-tandem mass spectrometry”, ***Applied Biological Chemistry***, 2017, 60(4)

Materials and Methods

Chemicals and consumables

HPLC grade acetonitrile (ACN) was purchased from Fisher Scientific (Seoul, South Korea), whereas formic acid (for mass spectrometry) and acetic acid (purity >99.7%) were from Sigma-Aldrich (St. Louis, MO, USA). QuEChERS extraction packets (4 g of magnesium sulfate ($MgSO_4$) and 1 g of sodium chloride (NaCl)), 2 mL dSPE tubes containing 25 mg of PSA and 150 mg of MgSO4, and dSPE containing GCB (2.5 and 7.5 mg) were obtained from Restek (Bellefonte, PA, USA). The other QuEChERS salt packages including AOAC and EN15662 methods were also from Restek. The ChloroFiltr dSPE tube (2 mL) containing PSA, $MgSO_4$, and 50 mg of ChloroFiltr was from UCT (Bristol, PA, USA). Ceramic homogenizers to aid extraction were purchased from Agilent Technologies (Palo Alto, CA, USA). Certified organic brown rice, orange, spinach, and potato for recoveries and real samples were obtained from several local markets, which is located in Seoul, Korea.

Analytical standard

Analytical reference (over 360 compounds), internal, and quality control standards with high purity (> 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), Chemservice (West Chester, PA, USA), Wako (Osaka, Japan), Dr. Ehrenstorfer (Augsburg, Germany), and Ultra Scientific (North Kingstown, RI, USA). Individual pesticide stock solutions (1000 µg/mL) were prepared in acetone or ACN, and then 20 groups of intermediate standard mixtures (containing about 20 pesticides for each group) were prepared at 50 µg/mL from each stock solution. Finally, working standard mixture at 2 μg/mL was used for matrix-matched calibration standards (0.01–1.0 μg/mL) by serial

dilution. An internal standard, tris(1,3-dichloroisopropyl)phosphate (TDCPP) was prepared at 0.5 μg/mL and the quality control (QC) standards mixture containing triphenyl phosphate (TPP), α-BHC-d_6, and chlorpyrifos-d_{10} were also prepared at 10 μg/mL.

Selection of GC column and instrumental conditions

GC-MS/MS analysis was carried out on a Shimadzu GCMS-TQ8040 triple-quadrupole system equipped with an AOC-20i autosampler (Kyoto, Japan). GC-MS solution software (version 4.3) was used for data processing. A solvent standard mixture (1 μL) at 0.1 μg/mL containing 360 analytes was injected onto narrowbore (Rxi-5Sil MS; 30 m × 0.25 mm i.d., 0.25 µm df) and microbore columns (Rxi-5SIL MS; 20 m × 0.18 mm i.d., 0.18 µm film thickness, df) installed in the same GC system, respectively. The oven temperature program for the narrowbore was as follows: 70 ℃ for 2 min, up to 160 ℃ at 15 ℃/min, and then to 260 ℃ at 5 ℃/min and finally to 300 ℃ at 15 ℃/min (held for 8 min). The program for microbore column was as follows: 50 ℃ for 1 min, increased to 200 ℃ at 25 ℃/min, then ramped to 300 ℃ at 10 ℃/min (held for 8 min). Total run time was 25.0 min with the microbore and 38.7 min with the narrowbore column. To effectively transfer the target analytes to the column, pulsed injection was employed at a pressure of 250 kPa with inlet temperature of 280 ℃. Helium (≥ 99.999%) was used as carrier gas at a constant flow (1.0 mL/min), and argon was used as collision gas. The ion source and transfer line temperature were 230 and 280 ℃, respectively. The electron ionization energy was -70 eV, and the detector voltage was set at 1.4 kV.

For MS/MS analysis, two transitions (quantifier and qualifier) were chosen for scheduled SRM mode after an automatic optimization procedure. The SRM detection window was ± 0.15 min and dwell times were adjusted

automatically on the basis of loop time (0.15 s) for the maximized data acquisition. Quantitation of individual compounds was performed using an internal standard based on peak area of quantifier transition. To choose a proper column for more efficient analysis, GC run time, peak shapes, and S/N ratios of representative pesticides obtained from the narrowbore column were compared with those from the microbore.

Automated adjustment of retention time (AART) and retention indices.

The conventional narrow bore column (30 m), the most popular capillary column in GC analysis, was replaced with a microbore column (20 m) in this study. Because retention times on the microbore column were different from those with the narrow bore column, the new retention times of the target analytes were calculated by adjusting the retention indices using the AART function in the GC/MS solution software.

To calculate the retention indices of target compounds, 1 μg/mL of *n*-alkane mixture solution containing hydrocarbons (C7-C32) was analyzed with the 30 m conventional narrow bore column. On the basis of the *n*-alkane retention times, the retention index of each analyte was calculated with the following non-isothermal Kovats retention index equation: (Choi et al., 2013; Lucero et al., 2009; Van Den Dool and Dec. Kratz, 1963).

$$\text{Retention index } = 100 \times \left(n + \frac{\log t_{R_{unknown}} - \log t_{R_{smaller\ alkane}}}{\log t_{R_{lager\ alkane}} - \log t_{R_{smaller\ alkane}}} \right)$$

Where n is the number of carbon atoms eluting immediately before the unknown compound, and $t_{R\ \text{smaller alkane}}$ and $t_{R\ \text{lager alkane}}$ are the retention times of n-alkanes eluting immediately before and after the unknown compound, respectively.

After changing the 30-m narrow bore column to a 20-m microbore

column, the *n*-alkane mixture was reanalyzed using modified GC conditions. By comparing the retention times of the *n*-alkane hydrocarbons from the two methods, new retention times of the target analytes were predicted using retention indices in the AART function.

Pulsed pressure injection (PPI) parameters.

PPI was employed for more effective transfer of target analytes onto the column. An experiment was conducted using the microbore column conditions to determine the optimum inlet pressure in order to increase peak sensitivity. One microliter of solvent standard mixture (50 ng/mL) was injected at inlet pressures of 180, 250, 300, and 350 kPa over 1.5 min, while a pressure of 142.4 kPa was the normal condition without PPI. The influence of PPI conditions on signal response was evaluated by comparing the average peak area and height of all target analytes.

Evaluation of peak sensitivity and column efficiency.

In order to compare peak sensitivities, the matrix matched standards solution (1 μL, 10 ng/g) of chili pepper, prepared by the modified QuEChERS method was injected into the GC-MS/MS using either the narrow bore or microbore column with three replicates. From the obtained chromatograms, parameters for peak sensitivity including peak height, width at half height (W_h), and signal-to-noise ratio (S/N) were calculated.

To assess the column efficiency, the matrix matched standards (10 ng/g) of chili pepper that was prepared by the modified QuEChERS method (Lee et al., 2017) were injected into GC-MS/MS using two methods (narrow bore *vs.* microbore). From the obtained chromatograms, the column efficiency including number of theoretical plate (*N*) and height equivalent to a theoretical

plate (*H*) were calculated as follows.

$$N = 5.545 \left(\frac{t_R}{W_h}\right) \text{ and } H = \frac{L}{N}$$

Where the W_h is the peak width at half-height and *L* referred to column length (mm). The W_h and *S/N ratios* were automatically obtained from the peak integration results in data processing software.

Optimization of sample preparation.

To optimize an extraction method, a preliminary test was performed with brown rice. The powdered sample (5.0 ± 0.1 g) fortified at 0.01 mg/kg (n=3) was extracted with different combinations of extraction solvents, salts, and buffers based on the QuEChERS method as follows. : (A) original method (ACN), (B) 0.1% formic acid in ACN, (C) 1% formic acid in ACN, (D) 0.1% acetic acid in ACN, (E) 1% acetic acid in ACN, (F) AOAC method (Lehotay, 2007), and (G) EN 15662 method (EN15662, 2008). For the cleanup procedure, general dSPE containing $MgSO_4$ and PSA was employed. Each final extract (400 μL) from seven different extraction methods was mixed with ACN (100 μL) for matrix-matched quantification. The extraction efficiency of each system was calculated on the basis of the matrix-matched standards employing single-point calibration (0.005 mg/kg).

For optimization of the dSPE cleanup, spinach containing a high amount of chlorophyll was used in comparison with several dSPE cleanup procedures. After spiking at 0.01 mg/kg, the homogenized spinach samples (*n = 3*) were extracted with ACN (0.1% formic acid) and partitioned by $MgSO_4$ and NaCl. After partitioning, the supernatants (1 mL) were transferred to four different dSPE sorbents as follows: (a) general dSPE (PSA only), (b) 2.5 mg of GCB, (c) 7.5 mg of GCB, and (d) 50 mg of ChloroFiltr. All dSPE sorbents

contained 25 mg of PSA and 150 mg of $MgSO_4$. Cleanup efficiency of each dSPE sorbent was calculated on the basis of the matrix-matched standards employing single-point calibration (0.005 mg/kg).

Final optimized sample preparation method

Frozen samples (brown rice, orange, spinach, and potato) were homogenized with dry ice into fine particles using a blender. The sample (10.0 ± 0.1 g) in a 50 mL centrifuge tube was fortified with pesticide standards at 0.01 and 0.05 mg/kg, and the QC standard (50 μL) at 10 μg/mL was also added for monitoring the extraction efficiency. For brown rice, deionized water (5 mL) was added to 5.0 ± 0.1 g of the powdered samples, allowing soaking for 1 h after fortification. ACN (10 mL) with 0.1% formic acid was added to each tube and the tubes were vigorously shaken (1500 rpm) using a Geno Grinder (1600 miniG SPEX Sample Prep, Metuchen, NJ, USA) for 1 min. Then, the tubes were cooled in an ice bath to prevent the thermal degradation of some pesticides due to $MgSO_4$ before the salt packet was added. After the mixture was shaken vigorously for another 1 min, the tube was centrifuged at 3500 rpm (5 min). The supernatant (1 mL) was transferred into a general dSPE tube and vortexed (1 min) on a Multi Speed Vortex (MSV-3500, Biosan, Riga, Latvia) before centrifugation at 15000 rpm (5 min). Finally, the supernatant (400 μL), ACN (50 μL), and an internal standard (TDCPP; 50 μL) at 0.5 μg/mL were transferred into a GC vial for GC-MS/MS injection. The final concentration of each sample was 0.8 g/mL (0.4 g/mL for brown rice).

Priming effects.

Untreated spinach (10 g) sample was prepared by the final optimized extraction procedure. After changing to a new deactivated liner, solvent standard mixtures (0.1 μg/mL) were analyzed by GC-MS/MS three times. Then, spinach extracts were injected with the same GC conditions for priming treatment, followed by solvent standard mixture injection again. The priming extracts and solvent standard mixture were injected alternately more than two times. The signal intensities obtained from six solvent standard mixtures and priming runs were compared to investigate the priming effect on inlet system.

Validation of analytical methods.

Method validation was conducted on the basis of the criteria of the document SANTE/11945/2015.(Hanot et al., 2015) The accuracy and precision of the optimized method were evaluated using mean recovery rate (%) and relative standard deviation (RSD, %) respectively, at fortification levels of 0.01 and 0.05 mg/kg. Because matrix components generally result in signal enhancement or suppression, matrix-matched standards are used to solve such problems by mixing solvent standard solution and blank matrix extracts. Therefore, in this study, the matrix-matched standards for calibration (1, 2.5, 5, 10, 25, 50, and 100 μg/kg) were prepared by adding the solvent standard solution, quality control and internal standards to blank matrix extracts. To minimize calculation error at low concentration, a weighting regression factor of 1/x was used for quantitation. Linearity and limit of quantitation (LOQ) were evaluated by each matrix-matched calibration. Matrix-dependent LOQ was determined to be the lowest concentration having an S/N ratio of a quantifier ion peak above 10.

Because errors can occur during sample preparation procedures including extraction, partitioning, and cleanup, three QC standards (TPP, α-BHC-d_6, and chlorpyrifos-d_{10}) were used as quality control of the data. When recoveries for the QC standards were in the range of 80–120% (Lozano, Kiedrowska, Scholten, de Kroon, de Kok and Fernández-Alba, 2016), the sample preparation was considered to be properly performed. TDCPP was used as an internal standard for quantitation.

Matrix effects (ME).

ME (%) was calculated as average percent suppression or enhancement by comparing the slope of the calibration curve of the matrix-matched standards with that of the solvent only calibration curve in ACN, using the following equation:

$$\text{ME, \%} = \left(\frac{\text{Slope of matrix matched calibration curve}}{\text{Slope of solvent only calibration curve}} - 1\right) \times 100$$

Results and discussion

Selected reaction monitoring (SRM) optimization

The total number of 360 pesticides was chosen after full scan and SRM optimization of initially selected 392 pesticides including several metabolites and isomers. A full scan spectrum of individual compound was obtained in the mass range of 50–500 *m/z*. Compounds of no detection (e.g., chloridazone, pymetrozine, cyromazine, TCMTB, and inabenfide) or poor response (lufenuron, fluoroimide, bistrifluoron, anilazine, trinexapac-ethyl, flupyradifuron, cycloprothrin, probenazole, allethrin, and bioresmethrin) or very low *m/z* value of base peak ion (73 *m/z*; methoprene) were excluded from the target analytes in this step.

On the basis of selectivity rather than signal intensity, specific precursor ions were then selected from the following ions: (1) the base ion with the highest intensity in the scan spectrum and (2) the ions with higher specificity to separate the target compound from other neighboring pesticides or interferences. For most of the target analytes, several ions could be potentially used as one of the precursor ions, but ions with the higher mass (*m/z* > 200) were preferred, whenever available, because those ions generally produced the highest S/N ratios for their product ions (Walorczyk, 2007) to give minimum matrix interferences. In general, the higher mass (*m/z*) for the precursor and product ions is generates a better S/N ratio (Fialkov et al., 2006; He, Chen, et al., 2015). The most selective and sensitive transition was used for quantifier and the second most selective for qualifier. In the selected target analytes, the diastereoisomers (17 pesticides) giving two or more peaks (e.g., cypermethrin, dimethomorph, and fenvalerate) were quantitated by the sum of each peak area. Interestingly, chlorobenzilate (*m/z* 325.2) and chloropropylate (*m/z* 339.2) were

not distinguished by SRM transitions due to the analogous structure (one methyl group differences) and patterns of fragmentation with the same retention time. The details of SRM transitions, collision energies and retention times for 360 pesticides are presented in **Supporting Information Table S1**.

Retention time adjustment by AART.

It is known that a column of smaller inner diameter (i.d.) and thinner film thickness (d_f) provides better separation and higher sensitivity than a wider column with thicker film. In this study, a microbore column (20 m × 0.18 mm i.d., 0.18 μm film thickness, d_f) was selected as a better alternative to a narrow bore column (30 m × 0.25 mm i.d., 0.25 μm d_f) for faster analysis with higher sensitivity. An analysis time of 35.2 min with the narrow bore column was greatly reduced to 17.8 min with the microbore column under optimal oven conditions. With the shortened analytical time, new retention times of all target compounds were predicted by the AART function

The AART function is capable of simultaneously adjusting the retention times of target compounds based on linear retention indices, which are constants for a given column phase and GC parameters (Kováts, 1958). Several studies have used linear retention indices as an identification tool for metabolite profiling (Choi et al., 2013; Lucero et al., 2009). However, few studies have reported an application case in which a large difference in column dimensions resulted in large retention time changes of numerous compounds.

After the retention time of each target analyte on the new microbore column was calculated by AART, it was compared with the actual retention time obtained from injection of a standard solution**.**

Figure 7. Distribution of retention time differences (predicted vs. observed retention times)

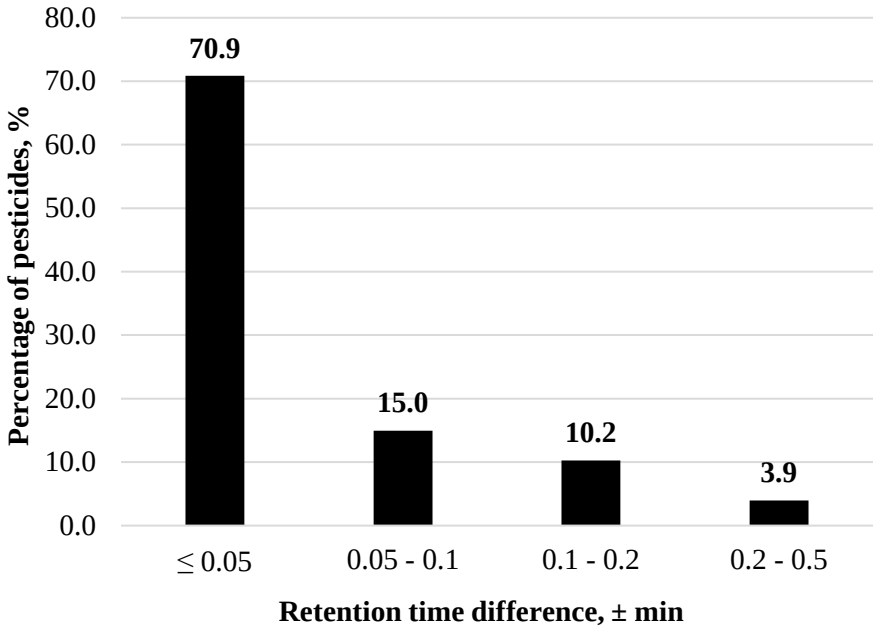

80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Percentage of pesticides, %
70.9
15.0
10.2
3.9
≤ 0.05
0.05 - 0.1
0.1 - 0.2
0.2 - 0.5
Retention time difference, ± min

Figure 7 shows the statistics of retention time differences between predicted *vs.* observed retention times of 376 peaks (356 pesticides). Most of the predicted retention times were consistent with the real analytical values; 70.9% of the target analytes had differences less than ± 0.05 min, indicating that extremely high accuracy was achieved over a wide range of retention times, even though the retention times were significantly reduced with the microbore column. For example, the predicted retention times of fenobucarb (6.933 min) and pirimiphos-ethyl (9.205 min) exactly matched their observed retention times.

Since AART operates by multipoint correction using many *n*-alkane hydrocarbon compounds of low to high boiling point, it gave extremely accurate results over the entire chromatographic range with many target compounds. Another retention time adjustment tool, retention time locking (RTL), works by a different mechanism whose purpose is to maintain a constant retention time by controlling the column flow when the same nominal column is changed or cut, using a locking compound (e.g., chlorpyrifos-methyl) (Almeida et al., 2007; Blumberg and Klee, 1998; Cook et al., 1999; Etxebarria et al., 2009). Retention time prediction by the AART function proved to be applicable to MRM method development in multiresidue analysis through improvement of efficiency and convenience.

Selection of GC Column

To find an efficient column in terms of better peak shape, sensitivity, and shorter analysis time, two columns of 30-m narrowbore (0.25 mm) (Chamkasem et al., 2013; Lehotay, Maštovská, et al., 2005; Li et al., 2009) and 20-m microbore (0.18 mm) were compared using solvent standard solution (mixture of 360 pesticides) at 0.1 μg/mL. The 20-m column saved 15 min of analysis time compared with the 30-m column based on the latest-eluting compound, as expected**. Figure 8** shows individual chromatograms of representative compounds (profuralin, fenthion, procymidone, and bifenthrin) obtained from the 30-m (**Figure 8-I**) and the 20-m column (**Figure 8-II**). The chromatograms from the 20-m column showed higher peak height and much higher S/N compared with the 30-m column conditions, resulting in much lower LOQ. Furthermore, despite the short run time (20 min) for 360 pesticides, sufficient data points (> 15) for each peak were obtained due to the fast scan speed. Judging from these results, the microbore column was chosen in this study for higher sensitivity and shorter run time.

Figure 8. SRM TIC of 360 pesticides at 0.01 µg/mL solvent standard mixture (a) and individual chromatograms of profuralin (b), fenthion (c), procymidone (d), and bifenthrin (e) corresponding to 30-m narrowbore (I) and 20-m microbore column (II).

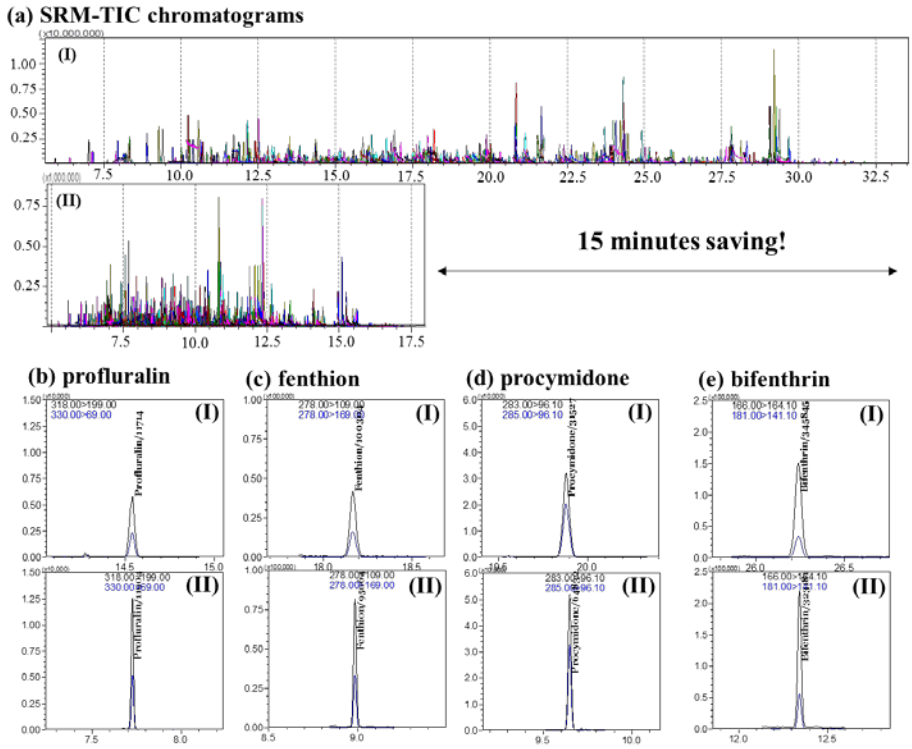
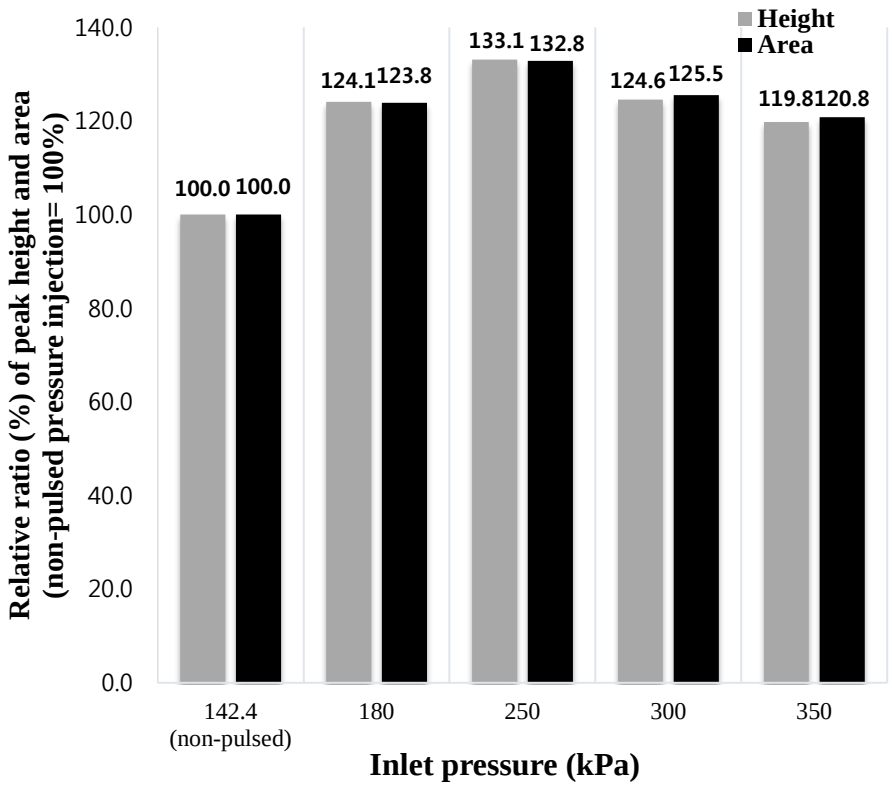

(a) SRM-TIC chromatograms
(I)
(II)
15 minutes saving!
(b) profluralin
(c) fenthion
(d) procymidone
(e) bifenthrin

Figure 9. Influence of pulsed pressure injection on average peak area and height of 356 target analytes (*n = 3*). A 50 ng/mL of solvent standard mixture (1 μL) was injected, and the results obtained from non-pulsed pressure injection were set to 100%.


Height
Area
Relative ratio (%) of peak height and area (non-pulsed pressure injection= 100%)
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
100.0 100.0
124.1 123.8
133.1 132.8
124.6 125.5
119.8 120.8
142.4 (non-pulsed)
180
250
300
350
Inlet pressure (kPa)

Effect of pulsed pressure injection (PPI)

PPI helps to effectively transfer target analytes into the column through an increased inlet injector pressure. In addition to increasing peak response, the optimum pulsed inlet pressure is also known to improve sample loading capacity and decrease matrix effects due to reduced time of interaction in the injector (Godula et al., 1999; Wylie, 1996). In order to optimize the pulsed pressure function of the inlet, relative peak areas and heights under various inlet pressures were compared with those of the microbore column.

Figure 9 shows average peak areas of 356 target analytes ($n = 3$) under various pulsed pressure conditions. The relative peak areas and heights (%) were expressed after normalization to non-pulsed pressure injection (142.4 kPa). As shown in **Figure 9**, an inlet pressure of 250 kPa gave the highest response of peaks, leading to increases of approximately 30% for peak area and height compared with no pressure injection. These results were consistent with previous studies, which showed that pulsed pressure injection under optimal inlet pressure conditions was useful for improving efficiency of sample injection (Cunha et al., 2009; Wylie, 1996). Also, it should be noted that the initial column oven temperature and volume of the inlet liner could affect the optimum pulse pressure (Zrostlíková et al., 2002).

Comparison of column efficiency.

Microbore column refers to the column that has the column inner diameter of range from 0.1 mm to 0.2 mm (Mastovská and Lehotay, 2003). The column can supply high linear velocity without high amount of carrier gas flow. This high linear velocity help to make the chromatographic band to sharp, providing high sensitivity by reduced resistance to mass transfer (Banerjee and Utture, 2015). To verify the feasibility of microbore column, the column efficiency was

evaluated by comparing results from 30 m narrow bore column.

Table 5 shows the column efficiency parameters of representative 20 compounds in terms of the number of theoretical plate (*N*), height equivalent to a theoretical plate (*H*), and signal-to-noise (S/N) ratio. Significantly higher S/N ratio were observed in 20-m micorobore column with narrower peak width (W_h) than 30-m narrow bore column. The widths at half height of the peak in microbore were reduced by half in comparison with those of narrow bore condition, meaning an increased chromatographic sensitivity.

The *N* is based on the peak sharpness (width) relative to time an analyte spends in the column. As an analyte retain longer in column and has narrower peak width, larger 'N' would be calculated, considered as high column efficiency. Likewise, the *H* is also another measure of column efficiency, calculated as column length (μm) divided by the *N*. In generally, the analytical condition having larger *N* and smaller *H* is regarded as good analytical performance.

In microbore column, most of pesticides gave remarkable column efficiency, especially in *N* indicated extremely higher than the acceptance criteria of system suitability (2000 > *N*) (Shabir, 2003). However, unexpected results were observed for late eluting compounds, which eluted at around 250 °C in both methods. These well-retained compounds such as butafenacil, etofenprox, azoxystrobin, and proparquizafop had inversely higher *N* value in 30-m narrow bore column than 20-m microbore column. This phenomenon can be explained by the long retention times more contributed to increase the N than the narrow peak width. Since the column length were reflected in *H* calculation, the plate height (*H*) were relatively higher in microbore than narrow bore column except for several compounds.

Table 5. Comparison of column efficiency for representative compounds using narrowbore vs. Microbore column ("N" means number of theoretical plate and "H" is height equivalent to a theoretical plate, *n = 3*)

No.	Compound Name	Narrowbore column (30 m × 0.25 mm, 0.25 µm)				Microbore column (20 m × 0.18 mm, 0.18 µm)			
		t_R	W_h[a]	*N*	*H*	t_R	W_h[a]	*N*	*H*
1	Dichlorvos	7.69	0.033	301,406	0.066	5.00	0.014	673,678	0.030
2	Heptenophos	11.50	0.038	514,370	0.039	6.76	0.014	1,230,781	0.016
3	Sulfotep	12.99	0.040	599,876	0.033	7.24	0.014	1,439,055	0.014
4	Iprobenfos	15.70	0.040	863,624	0.023	8.13	0.017	1,339,658	0.015
5	Pirimiphos methyl	17.41	0.043	877,678	0.023	8.70	0.017	1,362,296	0.015
6	Metolachlor	17.98	0.053	637,185	0.031	8.93	0.022	930,651	0.021
7	Chlorflurenol-methyl	20.11	0.046	1,049,103	0.019	9.74	0.021	1,281,405	0.016
8	Fenamiphos	21.10	0.042	1,407,950	0.014	10.12	0.018	1,807,812	0.011
9	p,p'-DDE	21.60	0.044	1,310,667	0.015	10.34	0.021	1,365,994	0.015
10	Fluazifop-butyl	22.53	0.045	1,384,990	0.014	10.68	0.020	1,579,732	0.013
11	Mepronil	23.59	0.048	1,338,423	0.015	11.16	0.022	1,468,352	0.014
12	Nuarimol	24.83	0.049	1,415,996	0.014	11.74	0.023	1,450,279	0.014
13	Pyridaphenthion	25.83	0.048	1,643,740	0.012	12.17	0.023	1,475,978	0.014
14	Bromopropylate	26.25	0.048	1,698,722	0.012	12.37	0.024	1,525,477	0.013
15	Clomeprop	26.96	0.048	1,761,211	0.011	12.70	0.023	1,694,757	0.012
16	Mirex	28.15	0.049	1,656,588	0.012	13.29	0.025	1,567,255	0.013
17	Butafenacil	29.88	0.037	3,583,957	0.006	14.28	0.024	1,961,550	0.010
18	Etofenprox	30.93	0.037	3,837,779	0.005	15.10	0.025	2,098,532	0.010
19	Azoxystrobin	32.87	0.044	3,090,335	0.006	16.50	0.026	2,243,707	0.009
20	Propaquizafop	35.28	0.055	2,333,851	0.009	17.88	0.033	1,642,736	0.012

[a]W_h: width at half the peak height

Enhancement of peak sensitivity on a microbore column with pulsed pressure injection.

Peak width at half peak height (W_h), peak height, and signal to noise (S/N) ratio for 20 representative compounds are shown in **Table 6**. The microbore column gave significantly higher peak height and narrower W_h compared with the narrow bore column. W_h on the microbore column was half that of the narrow bore conditions, demonstrating increased chromatographic efficiency. As a consequence, the relatively higher peak height led to a greater S/N ratio for most of the compounds, suggesting that a lower limit of detection or quantitation could be achieved. It was also observed that the use of PPI at an optimized pressure of 250 kPa with the microbore column further increased the peak height and S/N ratio by about 30%, a 2-3-fold enhancement of sensitivity compared to the narrow bore column without PPI. In the best case of the late eluting compound etofenprox, the S/N ratio significantly increased more than 9 fold.

Table 6. Comparison of peak width, height and S/N ratio for representative compounds using narrow bore vs. microbore column [with or without PPI (n=3)]

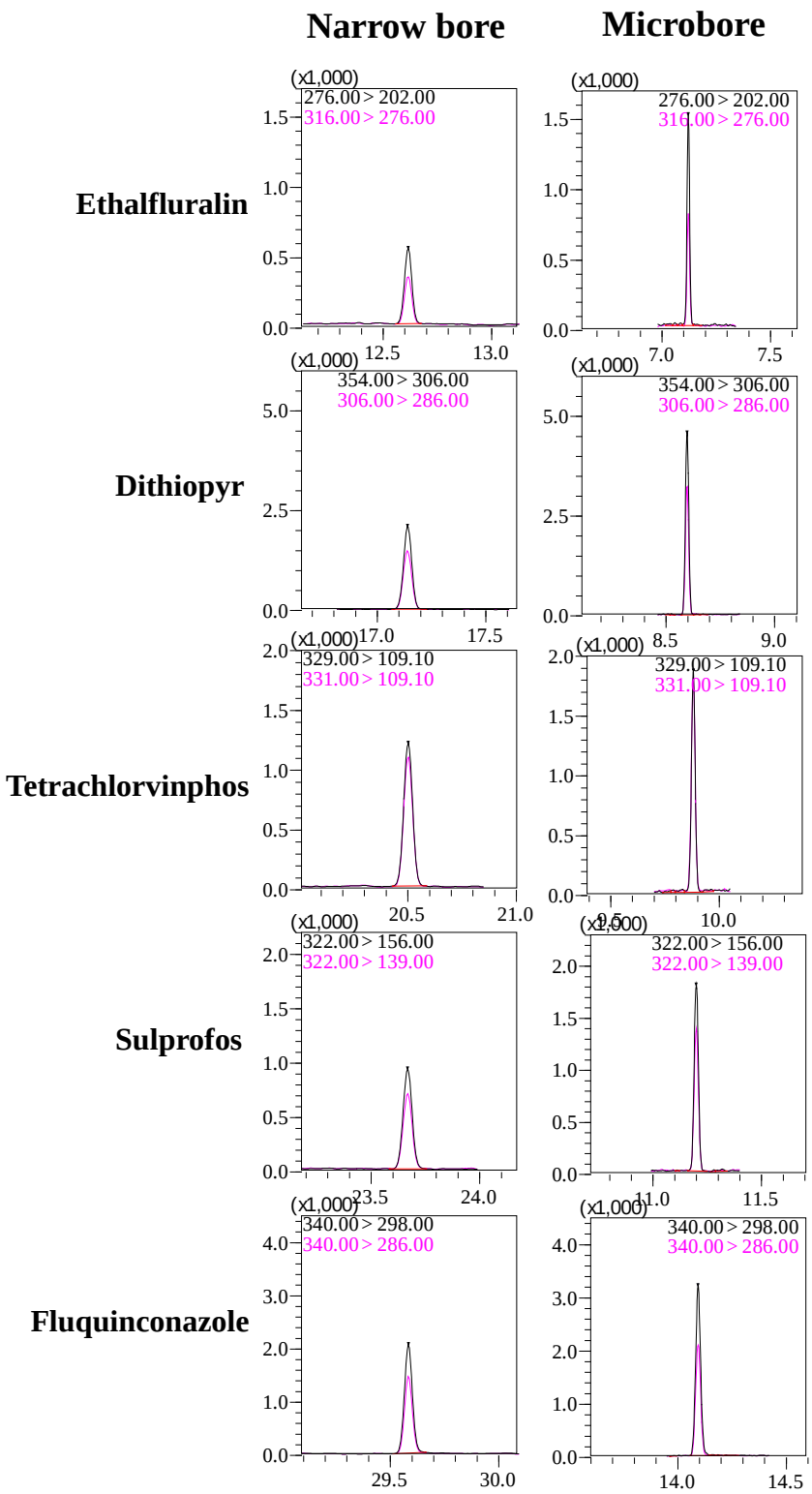
No.	Compound Name	Narrow bore column (without PPI[c])				Microbore column					
		t_R (min)	W_h[a] (min)	Height	S/N[b]	t_R (min)	W_h[a] (min)	without PPI[c]		with PPI[c]	
								Height	S/N[b]	Height	S/N[b]
1	Dichlorvos	7.69	0.043	677	111	5.00	0.016	1,373	153	2,227	206
2	Chloroneb	10.65	0.047	1,803	205	6.44	0.014	3,110	249	4,872	262
3	Trifluralin	12.86	0.040	1,040	96	7.19	0.014	2,926	278	4,802	349
4	Terbufos	14.67	0.043	1,726	159	7.78	0.036	3,759	268	6,467	353
5	Iprobenfos	15.70	0.043	2,713	248	8.13	0.017	5,917	307	9,925	559
6	Dichlofenthion	16.22	0.063	2,666	204	8.30	0.017	4,827	424	7,834	483
7	Fenitrothion	17.47	0.086	540	48	8.74	0.037	1,660	137	2,621	194
8	Metolachlor	17.98	0.056	3,478	414	8.93	0.022	5,935	458	9,714	581
9	Parathion	18.29	0.044	327	37	9.03	0.018	1,051	70	1,704	162
10	Procymidone	19.89	0.046	1,199	86	9.65	0.040	1,628	115	2,735	150
11	o,p'-DDE	20.45	0.046	2,355	142	9.88	0.020	3,625	240	5,812	449
12	Mepanipyrim	20.85	0.094	3,530	218	10.02	0.025	5,555	317	8,115	515
13	Azaconazole	21.96	0.099	3,777	65	10.50	0.047	6,640	164	9,817	265
14	Ethion	23.10	0.047	1,833	108	10.95	0.021	4,229	141	6,419	337
15	Mepronil	23.59	0.047	1,991	170	11.16	0.022	3,432	307	5,283	358
16	Fenazaquin	26.86	0.049	5,682	52	12.65	0.024	10,200	116	15,085	168
17	Cyhalofop-butyl	27.86	0.055	2,530	163	13.10	0.024	5,094	380	7,328	472
18	Fluquinconazole	29.59	0.048	1,299	61	14.09	0.025	2,210	232	3,146	280
19	Etofenprox	30.93	0.037	11,477	25	15.10	0.025	14,832	194	21,532	234
20	Pyraclostrobin	31.74	0.038	743	22	15.72	0.026	3,367	82	4,467	92

[a]W_h: width at half peak height, [b]S/N: signal to noise ratio, [c]PPI: pulsed pressure injection at 250 kPa

Figure 10 shows GC-MS/MS chromatograms of representative compounds (ethalfluralin, dithiopyr, tetrachlorvinphos, sulprophos, and fluquinconazole) on 30-m conventional and 20-m microbore columns when 10 ng/g of matrix-matched standard solutions prepared using chili pepper were injected. Chromatographic peaks of these compounds obtained with the microbore column showed relatively narrower and sharper peak shapes than those from the conventional column. It should be noted that extremely narrow band of chromatographic peak should be supported by high data record because the peak which is eluted within short time may not allow enough data points across the peak areas. The insufficient data points may lead to increase deviation of peak area (Mastovská and Lehotay, 2003) which can affect accurate quantitation. In this study, the enough data points over 15 across any peaks were available due to fast scan rate of GC-MS/MS.

In conclusion, compared to a 30-m narrow bore column, employing a microbore analytical column with the PPI function led to an improvement in peak sensitivity and a shorter analytical time.

Figure 10. Representative GC-MS/MS chromatograms on a 30-m narrow bore vs. a 20-m microbore column.


Narrow bore
Microbore
Ethalfluralin
Dithiopyr
Tetrachlorvinphos
Sulprofos
Fluquinconazole
(x1,000)
276.00 > 202.00
316.00 > 276.00
354.00 > 306.00
306.00 > 286.00
329.00 > 109.10
331.00 > 109.10
322.00 > 156.00
322.00 > 139.00
340.00 > 298.00
340.00 > 286.00

Priming effects

In the GC system, it is typically observed that the target molecules in solvent standards could be adsorbed to the active sites (e.g., silanol group) of a liner or column, causing low responses.(Schenck and Lehotay, 2000) As a different technology from analyte protectants, the DG SANTE guideline (Hanot et al., 2015) recommended that, after a new column or a new inlet liner is installed, a couple of matrix-matched blanks should be injected before running matrix-matched standards because the blank would deactivate the GC system, leading to the maximized transmission of target compounds to the detector. This phenomenon occurs due to “priming effects”, where matrices in the samples can mask the active sites of a new column or inlet liner.(Patel et al., 2005; Schenck and Lehotay, 2000) In this study, solvent standards and blank spinach and orange extracts were injected into the GC system after a new inlet liner (deactivated) was installed to evaluate the practical priming effect. The results showed that when the standard mixture was injected after the spinach extract injections, the peak responses of all the target compounds increased compared with that from the first injection after a new liner was installed (**Figure 11**); however a priming effect was not observed after the orange extract injections (**Figure 12**). These findings indicated that the active sites in a new GC liner seemed to be effectively masked by chlorophyll or other ingredients with nonvolatile property. It should be also noted that the increased peak response was maintained over the analysis time even after one priming injection. Therefore, a priming injection after a liner change is essential to achieve analytical results with higher sensitivity and precision. In this study, a priming injection with spinach extracts was always applied after a GC liner was changed.

Figure 11. Priming effects after replacing a new inlet liner in GC: relative peak area of solvent standard mixture (0.1 mg/kg) before (gray bars) and after (dark gray bars) spinach extract injections. The intensities were compared after each area was normalized by the area of the first injection as 100%. The top arrow indicates the sequence of sample injection.

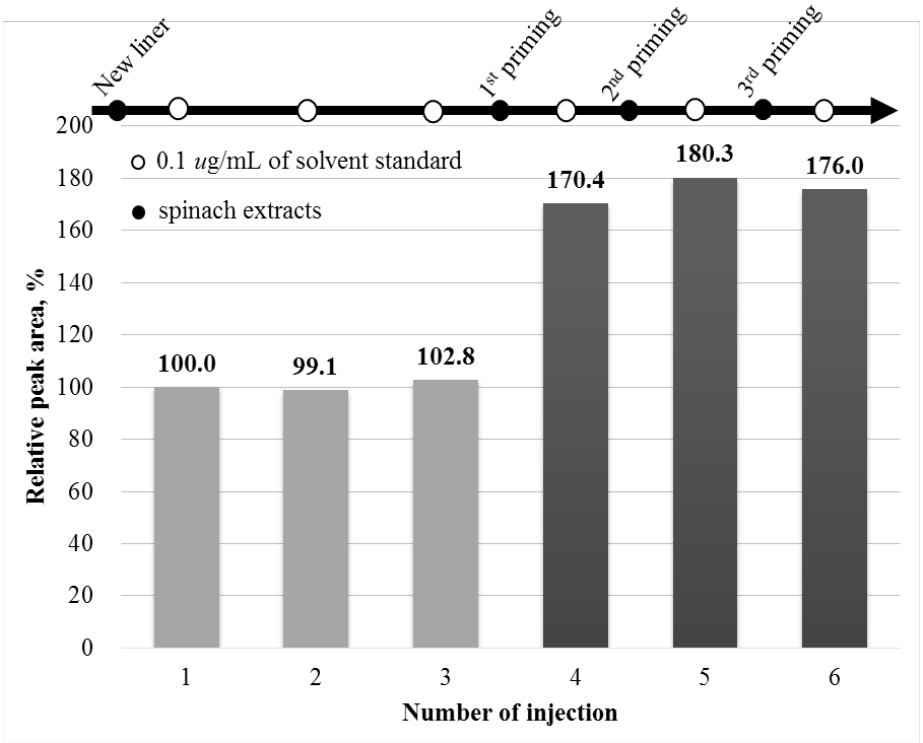
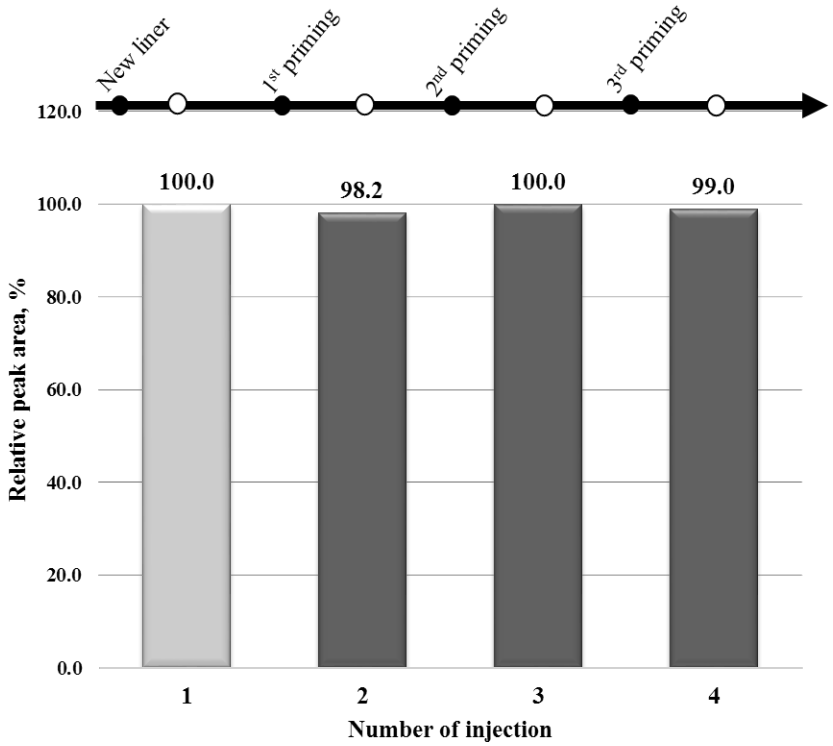

New liner
1st priming
2nd priming
3rd priming
0.1 ug/mL of solvent standard
spinach extracts
Relative peak area, %
200
180
160
140
120
100
80
60
40
20
0
100.0
99.1
102.8
170.4
180.3
176.0
1
2
3
4
5
6
Number of injection

Figure 12. Relative peak area of solvent standard mixture at 0.1 mg/kg after orange extracts were injected for priming effects. Average peak area of 360 pesticides in the first injection after replacing a new liner was set to 100%.


New liner
1st priming
2nd priming
3rd priming
120.0
100.0
98.2
100.0
99.0
100.0
80.0
60.0
40.0
20.0
0.0
Relative peak area, %
1
2
3
4
Number of injection

Modification of Sample Extraction Solvent.

Citrate (EN15662)(EN15662, 2008) and acetate buffered QuEChERS methods (AOAC 2007.1)(Lehotay, 2007) are usually used to efficiently extract hundreds of pesticides including base-sensitive pesticides, and several modified QuEChERS methods were also reported (Bresin et al., 2015; Grande-Martínez et al., 2016; He, Chen, et al., 2015; Rizzetti et al., 2016). Formic as well as acetic acid (Lehotay, Maštovská, et al., 2005) was used as an additive in extraction solvent to protect pH-sensitive pesticides (Koesukwiwat et al., 2011; Sack et al., 2015; Vázquez et al., 2015). In addition, several studies used formic acid to stabilize the pesticide in standard working solution or final extracts (Cho et al., 2016; Koesukwiwat et al., 2011; Walorczyk, 2008; Walorczyk et al., 2015a). In this study, therefore, addition of formic acid to extraction solvent was evaluated to increase the recovery efficiency of the target pesticides.

Table 7 shows the ratio of pesticides, that satisfied the recovery ranges between 70 and 120% with RSD $\leq$ 20% in the applied extraction procedures. Original method A, 0.1% formic acid method B, and citrate buffered method G showed relatively better recoveries and repeatability than the others did. No great differences in the number of analytes with satisfactory rates were observed, showing 93.6% (337 analytes) from method A, 93.9% (338 analytes) from method B, and 93.6% (337 analytes) from method G.

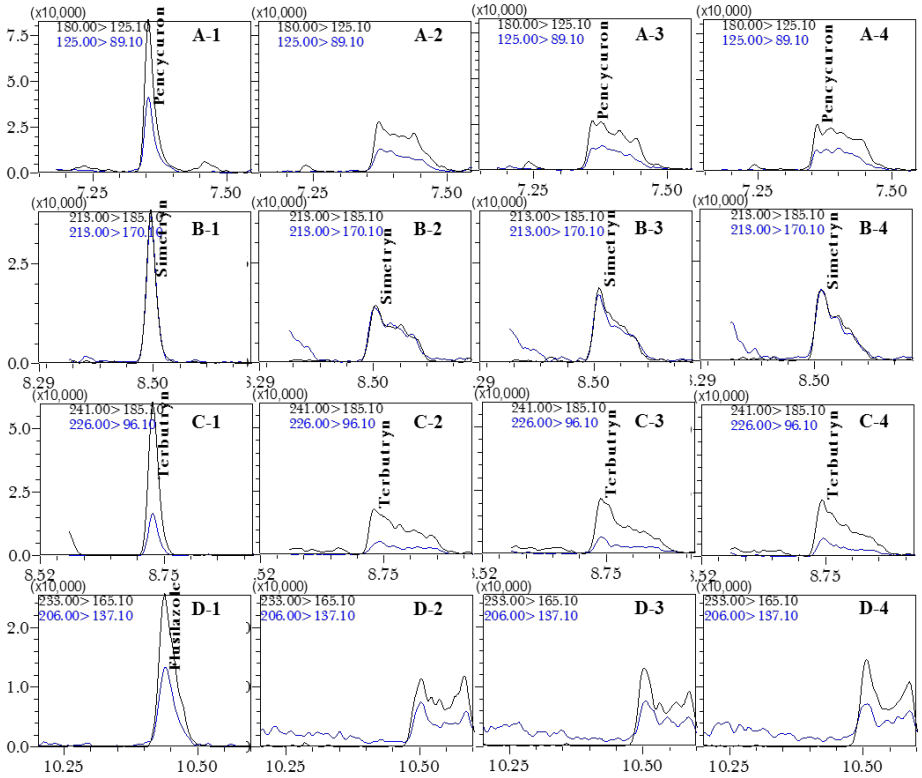
Table 7. Number of Pesticides and Percentages with Recoveries between 70 and 120 % with RSD ≤ 20% in Recovery Results from Different Extraction Solvents for Brown Rice Sample (Spiked at 0.01 m/kg, *n* = 3)

Method	Extraction solvent	Added salts and buffers in partitioning	No. of analytes	% of analytes
A	ACN	4 g of $MgSO_4$ and 1 g of NaCl	337	93.6
B	0.1% formic acid in ACN		338	93.9
C	1% formic acid in ACN		297	82.5
D	0.1% acetic acid in ACN		321	89.2
E	1% acetic acid in ACN		295	81.9
F	1% acetic acid in ACN	1.5 g of sodium acetate and 6 g of $MgSO_4$	286	79.4
G	ACN	4 g of $MgSO_4$, 1 g of NaCl, 1.5 g of trisodium citrate dehydrate, and 0.5 g of disodium hydrogen citrate sesquihydrate	337	93.6

On the other hand, ACN extract with 1% formic or 1% acetic acid gave undesirable tailing peaks for some compounds such as penycuron, simetryn and terbutryn. Flusilazole exhibited broad peaks (**Figure 13**) with unstable recoveries. This result was consistent with the previous studies, reporting that PSA may react with acid rather than absorb matrix interferences (Jadhav et al., 2015; Lehotay, Maštovská, et al., 2005). A high amount of acid in extraction solvent possibly prevented PSA from removing matrix interferences, leading to deterioration of peak shapes.

Base-sensitive pesticides such as tolylfluanid, dichlofluanid, and chlorothalonil, still showed poor recoveries despite lowered pH in extraction solvent by the AOAC method and 1% acetic or formic acid. For example, recoveries of tolylfluanid from the AOAC method and 1% formic and acetic acid (25.3, 18.4, and 26.4%, respectively) were slightly higher than those from other extraction solvents (< 10%) but still gave poor recoveries (< 30%). Therefore, ACN with 0.1% formic acid was selected as optimized extraction solvent because the appropriate amount of formic acid in extracting solvent was expected to give stable and consistent results for applying various sample types without additional buffer salts.

Figure 13. SRM chromatograms of pencycuron (A), simetryn (B), terbutryn (C) and flusilazole (D) in different extraction solvents: (1) 0.1 % formic acid; (2) 1% formic acid; (3) 1% acetic acid; (4) 1% acetic acid with AOAC buffered methods at 0.01 mg/kg spiking


(x10,000)
180.00>125.10
125.00>89.10
A-1
Pencycuron
A-2
A-3
A-4
213.00>185.10
213.00>170.10
B-1
Simetryn
B-2
B-3
B-4
241.00>185.10
226.00>96.10
C-1
Terbutryn
C-2
C-3
C-4
233.00>165.10
206.00>137.10
D-1
Pasilazole
D-2
D-3
D-4

Optimization of Sample Cleanup with dSPE

After extraction solvent was optimized as above, various dSPE sorbents were tested for optimum cleanup. Several types of dSPE in QuEChERS are generally adopted as cleanup procedures for robust and simple pesticide analysis. Green samples with a high amount of chlorophyll (e.g. lettuce, spinach or tea) are challenging in multipesticide analysis because the chlorophyll in the final extracts may cause chromatographic problems as well as increased GC maintenance cost (Walorczyk and Drożdżyński, 2012; Walorczyk et al., 2015a). To remove pigments such as chlorophyll, GCB sorbent has been used (Chen et al., 2016; Hayward et al., 2015; Hou et al., 2016; Koesukwiwat et al., 2010; Li et al., 2009) and recently, ChloroFiltr was introduced for the same purpose (Aznar et al., 2016; Walorczyk et al., 2015a). In this study, using spinach (a representative green sample) extract with ACN with 0.1% formic acid, four different types of dSPE sorbents were investigated to compare their effectiveness in terms of removing coextractives from green matrices, chromatographic separation, and recoveries. As expected, it was observed that the green color of chlorophyll was greatly decreased in final extracts by GCB or ChloroFiltr (**Figure 14**). As it treated by more GCB, the more light green appeared in color. The cleanup with chloroFiltr was also effective to eliminate the pigments.

Although it can be remove pigment like chlorophyll but at the same time, recoveries of some pesticides including planar pesticides (e.g., chinomethionat, coumaphos, cyprodinil, dimethipin, hexachlorobenzene, and pentachlorothioanisole) were greatly reduced (**Table 8**). This result was consistent with previous studies, showing that GCB interacted with not only chlorophyll but also planar structure pesticides (Anastassiades, Lehotay, et al., 2003; Hayward et al., 2015; Koesukwiwat et al., 2010; Mol et al., 2007). The

planar solvents (e.g., toluene) are known to enhance the recoveries of planar pesticide in GCB cleanup (Lehotay, Maštovská, et al., 2005; Mol et al., 2007; Wong et al., 2010), but the undesirable matrix impurities may be also extracted (Shimelis et al., 2007). Furthermore, it should be noted that the addition of a large amount of acid can have an even larger effect on the cleanup procedure than toluene, as shown by Lehotay and co-authours (Lehotay, Mastovska, et al., 2005). After ChlorFiltr cleanup, some pesticides such as bendiocarb, edifenphos, ethiofencarb, formothion, pentachlorothioanisole, and quintozene were not even recovered, and many compounds showed deteriorated peak shapes possibly due to interference from ChlorFiltr. If those pesticides are not target analyte in the analysis, GCB or ChloroFiltr can be used as an effective chlorophyll remover.

Considering acceptance criteria for accuracy and precision (70−120%, RSD ≤ 20 %), the general dSPE containing PSA gave a slightly higher satisfactory ratio for overall pesticides. The percentage of acceptance criteria was 93.8% in the PSA only, followed by 2.5 mg of GCB with PSA (92.2 %), 7.5 mg of GCB with PSA (85.5 %), and ChloroFiltr with PSA (74.5 %).

Figure 14. Final extracts after cleanup by different cleanup absorbents : (A) extract with 25 mg of PSA; (B) extract with 25 mg of PSA and 2.5 mg of GCB; (C) extract with 25 mg of PSA and 7.5 mg of GCB; (D) extract with 50 mg of PSA and ChloroFiltr

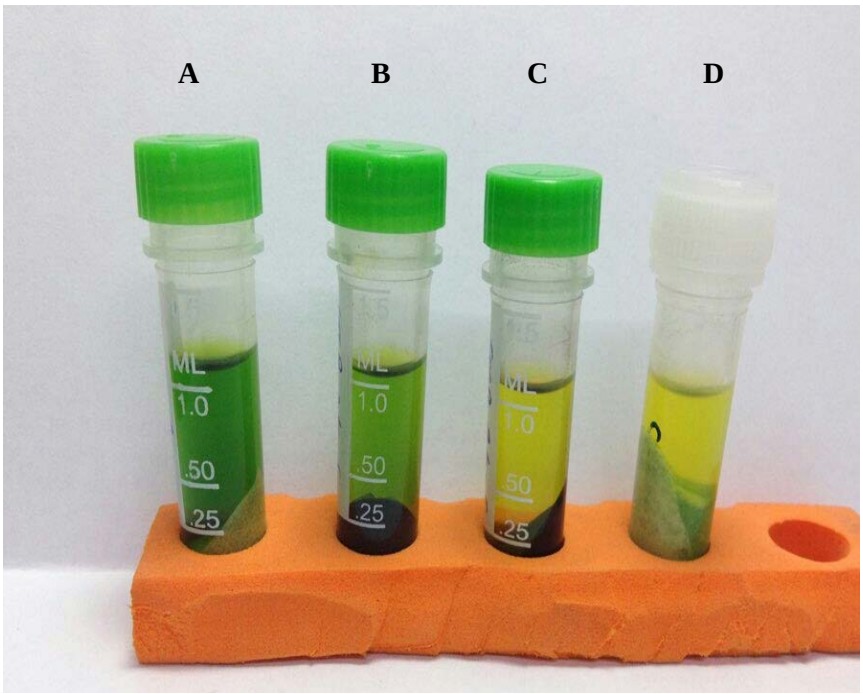

A
B
C
D
ML
1.0
.50
.25

Table 8. Recovery Results for Representative Pesticides Including Planar Pesticides in Spinach Matrix (0.01 mg/kg Spiking Level, n = 3) from Cleanup with Different Types of dSPE Sorbents

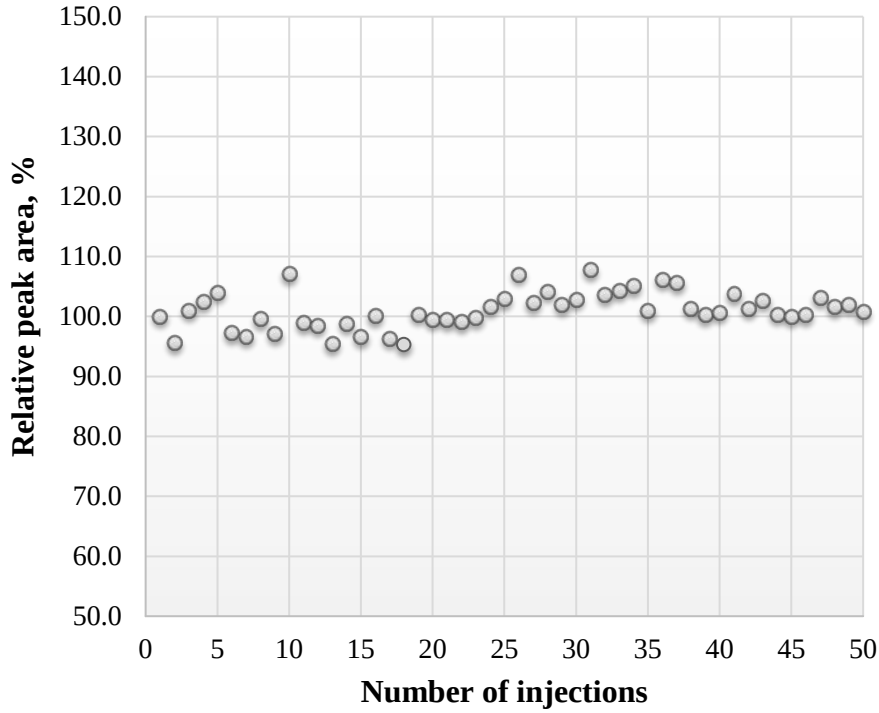
Pesticdes	Recovery, % (RSD, %)			
	PSA	PSA+2.5 mg GCB	PSA+7.5 mg GCB	PSA+50 mg ChloroFiltr
Bendiocarb	49.1 (16.3)	44.7 (22.2)	32.6 (36.9)	-[a]
Carbofuran	107.5 (3.9)	96.3 (4.4)	90.3 (5.3)	81.1 (5.7)
Chinomethionat[b]	70.7 (8.5)	60 (16.9)	26.9 (27.6)	41.3 (51.5)
Chlorothalonil[b]	100.7 (7.8)	87.4 (6.2)	72.3 (12.9)	58.6 (19.5)
Coumaphos[b]	99.3 (1.3)	94.1 (3.1)	80.9 (11.4)	81.6 (16)
Cyprodinil[b]	102.5 (3.3)	97.3 (3.8)	91 (4.1)	61.5 (7.7)
Ddimethipin[b]	84.4 (7.9)	84.5 (16.3)	76.3 (4.9)	65.7 (3.9)
Edifenphos	98 (8.4)	73.3 (7.1)	54.6 (44)	-[a]
Ethiofencarb	81.9 (5)	68 (13.8)	44.1 (29.9)	-[a]
Formothion	83.1 (4.6)	56.3 (27)	47.3 (21.2)	-[a]
Hexachlorobenzene[b]	87.7 (5.4)	77.5 (11.9)	68.3 (16.1)	83.1 (0.7)
Pentachlorothioanisole[b]	77.3 (6.8)	64.7 (22.7)	65.5 (22.6)	-[a]
Quintozene[a]	83.1 (5.6)	69.8 (12.2)	58.4 (23.7)	-[a]
% of pesticides (70-120%, ≤20% RSD)	93.8	92.2	85.5	74.5

[a]Pesticides that could not be quantitated due to matrix interference.

[b]Planar structure pesticides.

To demonstrate whether the remaining chlorophyll and interferences in the sample extract affect analysis after the simple general dSPE containing PSA cleanup, spinach samples (0.01 mg/kg of matrix-matched standard) were injected into GC 50 times, consecutively. The results (**Figure 15**) showed that the average area of 360 pesticides was not changed with 3.0% of RSD. These data indicated that coextractives (chlorophyll) from the spinach would not affect repeatability or recoveries in routine analysis as Lehotay *et al*. reported that the chlorophyll had no influence on the GC-MS analysis (Lehotay, Maštovská, et al., 2005). Furthermore, it was expected that chlorophyll in extracts may help to keep the priming effects mentioned above. As a result, it was confirmed that the general dSPE containing PSA and $MgSO_4$ was the best cleanup option for this multiresidue analysis. Finally, the general dSPE was used for method validation in this study.

Figure 15. Distribution of relative peak area (average of 360 analytes) during 50 consecutive injections of spinach matrix matched standard at 0.01 mg/kg.


150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
Relative peak area, %
0
5
10
15
20
25
30
35
40
45
50
Number of injections

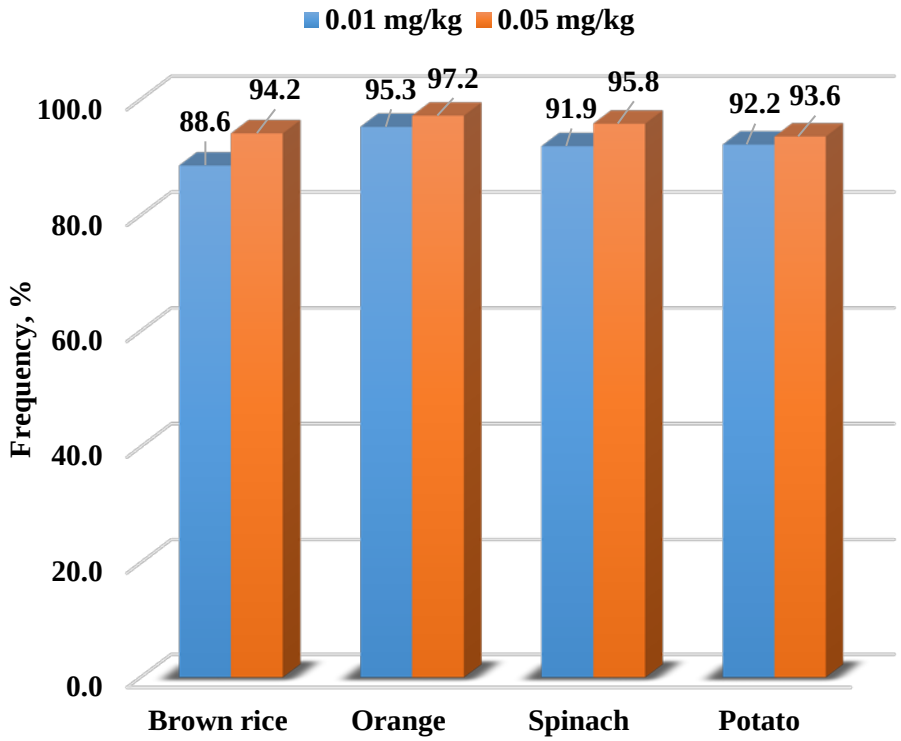
Method Validation. To validate the optimized sample treatment method (ACN with 0.1% formic acid extraction and cleanup with the general dSPE containing PSA and $MgSO_4$), recoveries of each compound were investigated by fortifying 360 pesticides into four untreated samples (brown rice, orange, spinach, and potato) at 0.05 and 0.01 mg/kg (n=6). Matrix-dependent LOQ and linearity (r^2) were calculated by matrix-matched calibration from each commodity (**Table S2**). For most pesticides (349, 344, 349, and 347 in brown rice, orange, spinach, and potato, respectively) of 360 compounds, LOQs were < 0.01 mg/kg. Twelve pesticides (binapacryl, captafol, captan, carbofuran, carbosulfan, cinmethylin, dichlofluanid, hexythiazox, imazalil, propargite, tolfenpyrad, and vernolate) were not separated properly due to matrix interference, degradation, and broad and tailing peak shape. Base-sensitive and thermally unstable compounds (e.g., captan, captafol, dichlofluanid, and imazalil) gave no detectable peaks at low concentration in all matrices, which was consistent with the results from previous studies (Jadhav et al., 2015; Koesukwiwat et al., 2011; Koesukwiwat et al., 2010; Lehotay, Maštovská, et al., 2005; Savant et al., 2010). The linear correlation coefficients (r^2) were > 0.99 within the range of 1−100 μg/kg for all of the pesticides except chlorothalonil, etridiazole, fluazinam, nitrapyrin, phenothrin, and problematic compounds mentioned in LOQ estimation.

On the Basis of the acceptability criteria of DG-SANTE guideline (Hanot et al., 2015), the recoveries in four commodities are summarized in **Figure 16**. The percentages (of 360 pesticides) satisfying the validation criteria (recovery; 70−120% with RSD ≤ 20%) were in the range of 88.6−95.3% (0.01 mg/kg level) and 93.6−97.2% (0.05 mg/kg level), indicating that excellent results were achieved. Details of the accuracy and precision data in all of the samples and analytes are also presented in **Table S3**.

Because of low sample amount (5 g) of brown rice compared to the other crop samples (10 g), recoveries from brown rice sample at the low spiking level (0.01 mg/kg level) showed a relatively low frequency (88.6%). For example, at the low spiking level in brown rice, some compounds such as bendiocarb, ethiofencarb, fosthiazate, phosphamidon, tetrachlorvinphos, and zoxamide gave low signal intensities, resulting in insufficient recoveries, however these pesticides at higher spiking level (0.05 mg/kg) were successfully quantified.

Apart from the problematic pesticides in LOQ estimation and linearity calculation, some pesticides including carbaryl, chlorothalonil, cafenstrole, cyflumetofen, and folpet gave lower recoveries in all of the crop samples. Chlorothalonil is known to be degraded in QuEChERS methods due to its base-labile property (Chamkasem et al., 2013; Lehotay, Maštovská, et al., 2005; Walorczyk and Drożdżyński, 2012) and it was reported that the ethyl acetate extraction or acetone extraction with EDTA as a stabilizing reagent could improve the recoveries of chlorothalonil (Belmonte Valles et al., 2012; Peruga et al., 2013). Carbamate pesticides (e.g., carbaryl and carbosulfan) easily break down on the GC injector, causing relatively low responses and unstable recoveries in GC-MS/MS. Therefore, it was concluded that these pesticides are more LC amenable as reported in the other studies (Lozano, Kiedrowska, Scholten, de Kroon, de Kok and Fernández-Alba, 2016; Mol et al., 2007; Morris and Schriner, 2015; Niell et al., 2014). Ethoxyquin and fluazinam also gave poor recoveries in all of the matrices except orange due to matrix interferences, as previously reported (Chen et al., 2016; Jadhav et al., 2015; Zhao, Feng, et al., 2014).

Figure 16. Percentages of pesticides satisfying the recovery rates of 70-120% and RSD≤20% at 0.01 and 0.05 mg/kg spike levels, using the optimized method in this study.


0.01 mg/kg
0.05 mg/kg
Frequency, %
100.0
80.0
60.0
40.0
20.0
0.0
88.6
94.2
95.3
97.2
91.9
95.8
92.2
93.6
Brown rice
Orange
Spinach
Potato

Real samples including domestic or imported agricultural produce (brown rice (5), spinach (3), oranges (4), and potatoes (5)), were analyzed using the optimized method. Of 360 pesticides, 14 pesticides were identified in 11 incurred samples (**Table 9**). No pesticide was detected in potato samples. The levels of pesticides identified in all samples were lower than MRLs by Korean legislation.(Korean Pesticides MRLs in Food; 2016;, 2016) Trace levels of several pesticides including azoxystrobin, difenoconazole, fenoxanil, tebuconazole, thifluzamide, triazophos, hexaconazole, and isoprothiolane were found in four brown rice samples. Dimethomorph was detected in all of the spinach samples (0.004−7.60 mg/kg). Indoxacarb was also found in one spinach sample with the highest concentration (0.81 mg/kg).

Table 9. The concentrations (mg/kg) of pesticides detected in real sample analysis.

Sample type	No.	Origin	Detected pesticides	Concentration (mg/kg)	MRL (mg/kg)
brown rice	1	Imported	azoxystrobin	0.007	1.0
			difenoconazole	0.017	20
			tebuconazole	0.019	0.05
			triazophos	0.011	0.05
	2	Imported	n.d.	-	-
	3	Domestic	azoxystrobin	0.007	1.0
			hexaconazole	0.010	0.3
	4	Domestic	hexaconazole	0.008	0.3
			isoprothiolane	0.056	2.0
	5	Domestic	fenoxanil	0.032	0.5
			hexaconazole	0.037	0.3
			thifluzamide	0.016	0.1
spinach	1	Domestic	azoxystrobin	0.057	20
			dimethomorph	7.601	20
	2	Domestic	dimethomorph	0.014	20
			indoxacarb	0.813	3.0
	3	Domestic	dimethomorph	0.004	20
orange	1	Imported	fluvalinate	0.008	0.01
	2	Imported	chlorpyrifos	0.031	0.3
	3	Imported	cypermethrin	0.007	2.0
	4	Imported	azoxystrobin	0.113	5.0
			chlorpyrifos	0.042	0.3
			difenoconazole	0.003	0.5
			fludioxonil	0.047	10
potato	1	Domestic	n.d.	-	-
	2	Domestic	n.d.	-	-
	3	Domestic	n.d.	-	-
	4	Domestic	n.d.	-	-
	5	Domestic	n.d.	-	-

* n.d.: no residues detected.

Matrix Effect (ME).

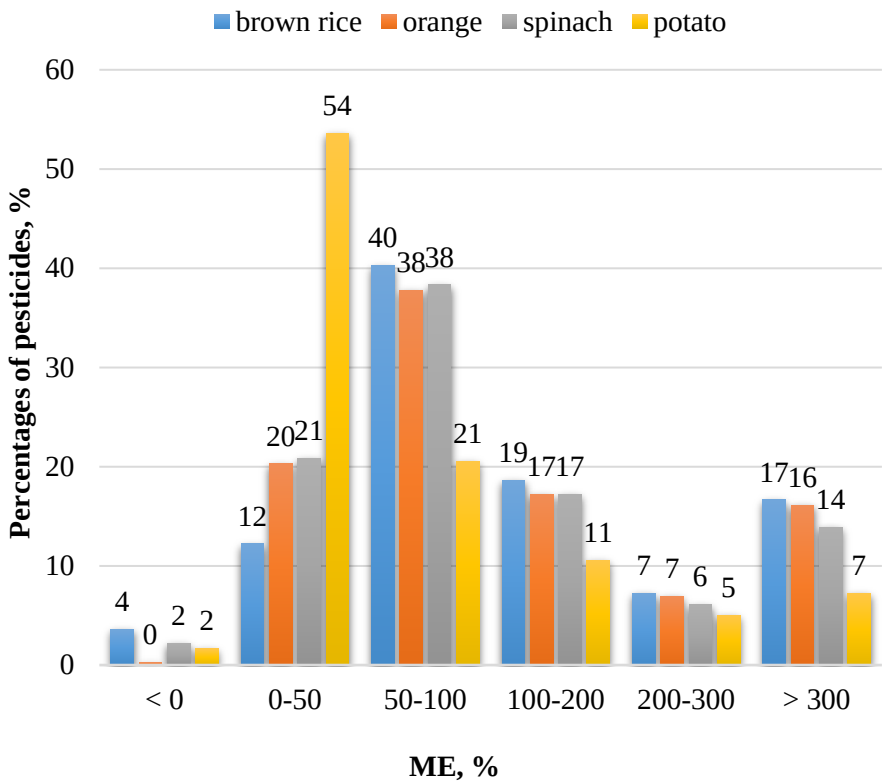
ME (%) is a major concern in GC-MS/MS because it has been observed significantly due to interaction between active sites of the liner or column and target analytes or matrix components. The ME depends on the nature of pesticide, extraction method, and analytical instrument as well as the sample matrix (de Sousa et al., 2012; Ferrer et al., 2011; Kittlaus et al., 2011).

To evaluate the ME, the slope of each matrix-matched calibration curve for individual pesticides was compared with that from the solvent-only calibration curve. A positive value of ME was considered as signal enhancement, whereas a negative value was considered as signal suppression. **Figure 17** shows the distribution of MEs of the target analytes in four matrices. Absolute values of ME are listed in **Table S3**. Except for a few pesticides, significant enhancement was observed for most of the target analytes in all the matrices. When the MEs are divided into several ranges (1−300%), many of the 360 pesticides analyzed in brown rice (40% of 360 pesticides), orange (38%), and spinach (38%) were in the 50−100% ME ranges. However, 54% of the target pesticides in potato were in the range of 0−50%, indicating relatively low MEs. This was also consistent with other studies showing that potato gave a relatively low ME in the GC analysis (Koesukwiwat et al., 2010; Uclés et al., 2014). Strong enhancements (> 100% of ME value) were observed for 43, 40, 37, and 23% of the target compounds in brown rice, orange, spinach, and potato, respectively. These results strongly confirmed the importance of matrix-matched calibration for proper quantitation of compounds.

High matrix effects in GC-MS/MS were not surprising as previous studies showed (Cho et al., 2016; Koesukwiwat et al., 2010; Lozano et al., 2014). Many active sites presented in the GC system might interact with analytes (e.g., silanol and metal ion), leading to decreased signal intensity. On

the other hand, matrix components could shield active sites and help to deliver pesticide to the GC detector. Consequently, increased peak intensities were obtained in matrix-matched standards. The use of analyte protectant (AP) has been known to compensate the matrix effect, providing improved peak intensity and shape. However, we did not use the AP because it requires an additional analytical step (adding AP solution) and specific management for a GC syringe to prevent contamination by AP; as well, it could increase undesirable complexity in chromatograms (Koesukwiwat et al., 2010). Because pesticide-free matrices or the exactly same matrix as the target sample is not always available for preparation of matrix-matched standards in routine analysis, AP would play an important role in decreasing matrix effects.

Figure 17. Distribution of matrix effects (MEs) in each commodity. The MEs were assessed by the slope ratios of the matrix-matched calibration curves to solvent-only calibration curves.


brown rice
orange
spinach
potato
60
50
40
30
20
10
0
Percentages of pesticides, %
4
0
2
2
12
20
21
54
40
38
38
21
19
17
17
11
7
7
6
5
17
16
14
7
< 0
0-50
50-100
100-200
200-300
> 300
ME, %

Part 2

Rapid and Simultaneous Analysis of 332 Pesticides in Brown Rice, Orange, and Spinach Using LC-MS/MS

Materials and Methods

Chemicals and Consumables

HPLC grade methanol (MeOH) and acetonitrile (ACN) was purchased from Fisher Scientific (Seoul, South Korea), whereas formic acid (purity > 99.7%) and ammonium formate (purity ≥ 99%) were from Sigma-Aldrich (St. Louis, MO, USA). QuEChERS salts packets containing 4 g of magnesium sulfate ($MgSO_4$) and 1 g of sodium chloride (NaCl), dispersive SPE tubes containing 25 mg of primary and secondary amine (PSA) and 150 mg of MgSO4, and dSPE containing GCB (2.5 and 7.5 mg) were obtained from Restek (Bellefonte, PA, USA).

High purity of analytical reference (309 compounds) standards were purchased from Sigma-Aldrich (St. Louis, MO, USA), Chemservice (West Chester, PA, USA), Wako (Osaka, Japan), Dr. Ehrenstorfer (Augsburg, Germany), and Ultra Scientific (North Kingstown, RI, USA). Individual pesticide stock solutions of 1000 μg/mL (100 µg/mL for carbendazim) were prepared in ACN or MeOH, considering each of the purity. After making a composite standard mixture containing 309 pesticides at concentration of 5 μg/mL by combining aliquot of individual stock solution, working standard solutions at the concentration of 1, 2, 5, 10, 20, 50, 100, 500, and 1000 μg/mL were prepared by serial dilution using ACN. For multiple reaction mornitoring (MRM) optimization, 1 μg/mL of individual standard solutions were also prepared in ACN. All standard solutions were kept at -20°C.

LC-MS/MS instrumentation

LC-MS/MS analysis was performed on a Shimadzu LCMS-8050 triple-quadrupole mass spectrometer (Kyoto, Japan) coupled with Nexera X2 ultra-

high pressure liquid chromatograph. A Phenomenex Kinetex C18 analytical column (10 cm × 2.1 mm i.d., 2.6 μm particle size) with 40 °C of column oven temperature was used for separation. The methanol-based mobile phase consisted of water (A) and methanol (B) containing 5mM ammonium formate and 0.1% formic acid was compared with acetonitrile-based mobile phase consisted of water (A) and acetonitrile (B) containing 0.1% formic acid with the following gradient program. Initially, the organic solvent mobile phase (B) was hold at 5% for 0.5 min, ramped to 55% B in 0.5 min, followed by a linearly increased to 95% B over 7 min, held for 3 min. Finally, it was ramped again to 100% B over 1 min, decreased to 5% B in 0.1min and maintained for 2.9 min (A total run time was 15 min). The flow rate was 0.2 mL/min and injection volume was 5 μL.

A scheduled multiple reaction monitoring mode using fast switching between positive and negative mode in electrospray ionization was employed to apply a large number of LC-MS/MS-amenable pesticides. The temperature parameters for heated ESI were interface temperature of 300°C, desolvation line (DL) temperature of 250°C, and heat-bock temperature of 400°C. The flow rate parameters for heating (air), nebulizing (N_2), and drying gas (N_2) were 10, 3, and 10 L/min (air), respectively. After automatic optimization procedure of MRM transitions, the best quantifier, qualifier ion, and collision energies (eV) were optimized by injections of individual compounds (1 μg/mL).

Final sample preparation procedure

The modified QuEChERS method based on ACN containing 0.1% formic acid for extraction solvent, that was previously validated was used for sample preparation procedure (Lee et al., 2017). An amount (10.0 ± 0.1 g) of homogenized samples (brown rice, orange, and spinach) by dry ice were

weighed into 50 mL of centrifuge tube. For brown rice, 5.0 ± 0.1 g were used and 5 mL of deionized water was added, and then soaking for 30 min. ACN (10 mL) containing 0.1% formic acid was added for extraction and vigorously shaken for 1 min on a Geno Grinder (1600 miniG SPEX Sample Prep, Metuchen, NJ, USA) at 1500 rpm. To minimize the heat release causing by moisture absorbing with $MgSO_4$, the tubes were cooled in an ice bath for a while. Furthermore, 4 g of anhydrous $MgSO_4$ and 1 g of NaCl were added into the tube and shaken for another 1 min. After centrifuged at 3500 rpm (5 min), the supernatant (1 mL) was transferred into a dispersive SPE tube (2 mL) containing 150 mg of anhydrous MgSO4 and 25 mg of PSA sorbent. The tubes was mixed on vortex mixer for 1 min before centrifugation at 15000 rpm (5 min). The supernatant (400 μL) were transferred into 2 mL of amber vial and added ACN (100 μL) for LC-MS/MS injection.

Validation of analytical method

Recovery experiments were carried out to validate the analytical method on brown rice, orange, and spinach sample. The Five replicates at two concentrations (10 and 50 ng/g) were conducted by fortifying pesticide mixture on each of three commodities. The trueness and precision of the optimized method were determined using average recovery rate (%) and relative standard deviation (RSD, %) respectively. Concentrations of each analytes were calculated by matrix-matched calibration to compensate matrix-induced signal enhancement or suppression. The matrix-matched standards for calibration (1, 2, 5, 10, 20, 50, and 100 ng/g) were prepared by adding the solvent standard solution to blank extracts, which was prepared with same procedure. Limit of quantitation (LOQ) was defined as the minimum concentration achieving the signal-to-noise (S/N) ratio of above 10 for quantifier ion in the solvent-only

standard calibration curve. Linearity of calibration curves were also evaluated by matrix-matched calibration.

Matrix effect

Matrix effects (ME, %) were was calculated by comparing the peak response of 100 ng/g within the matrix-matched standards (brown rice, orange, and spinach) and solvent-only standards using the following equation:

$$\mathrm{ME}, \% = \left(\frac{\text{peak area of matrix matched standard}}{\text{peak area of solvent} - \text{only standard}} - 1\right) \times 100$$

A negative value of matrix effect indicates signal suppression, a positive value indicates signal enhancement in matrix contained environment.

Results and discussion

MRM optimization

To achieve best signal intensity in LC-MS/MS, the MRM transitions were optimized by injection of individual standard solution (1000 ng/g) without passing through an analytical column. First of all, a full scan spectrums of each compounds were obtained in the mass range of 50 to 1000 m/z using quadrupole 3 (Q3) scan with the switching positive/negative ionization. Considering the signal intensity, the most abundant ion were selected as a precursor ion for each of analytes. Most of the pesticides were easily ionized by positive mode, forming $(M+H)^+$ ion, whereas ammonium adduct form of $(M+NH_4)^+$ were chosen as precursor ion in the ten pesticides (e.g., oxamyl, flumiclorac-pentyl, butafenacil, and deltamethrin). The sodium adducts forming (M+Na)+ were only found for two pesticides (butocarboxim and pyribenzoxim). Eighteen compounds (e.g., bentazone, haloxyfop, lufenuron, and hexaflumuron) were more suitable for negative ionization mode than positive mode. Then, different collision energies were automatically tested to obtain the corresponding product ions with higher sensitivity at the range of 0-50 eV. The highest transition in sensitivity was used for quantifier and the second most selective transition for qualifier. The detail MRM transitions of each pesticides including retention times are listed in **Table S4** in the supplemental data online.

Selection of mobile phase

Ammonium formate has been widely used mobile phase additives as a donor of ammonium ion. With the limitation that low solubility in acetonitrile, most of method use ammonium formate with methanol for mobile phase. Even though it has been reported that ammounium formate with acetonitrile is capable to apply for mobile phase (Bordin et al., 2017), the heating is needed to dissolve ammonium formate. Also, from our experience, the insoluble ammonium formate residue could potentially block spray needle in LC-MS/MS, leading to increase the maintain cost. On the other hand, acetonitrile is often used for mobile phase with advantage of strong elution strength and providing lower pressure in analytical column.

Because methanol is capable of applying ammonium formate and acetonitrile is not, the effects on peak sensitivity in different combinations of mobile phase were studied. The result was compared by relative peak area as shown in **Figure 18**. Many compounds showed higher intensities in methanol-based mobile phase, whereas only 44 compounds had higher peak area in acetonitrile-based mobile phase. Average 250% of peak area were increased in methanol-based mobile phase. Relatively high peak response of the methanol-based mobile phase could be attributed to increased ionization efficiency by the addition of ammonium formate. As expected, the molecules that was ionized to ammonium adducts showed greatly reduced peak area by the absence of ammonium formate. Moreover, four pesticides, i.e. cycloprothrin, deltamethrin, famoxadonen, and lactofen were not even detected in acetonitrile-based mobile phase. On the basis of these results, methanol and water containing 5 mM annonium formate and 0.1% formic acid each were selected as mobile phase for LC-MS/MS analysis.

Optimization of injection volume

The relationship between injection volume and precision was studied to acquire reliable quantitation. To eliminate deviation on data processing, representative 180 compounds that gave symmetric peak with distinct signal intensity were selected. **Figure 19** summarizes the average peak area of target compounds and repeatability results obtained from different concentration and injection volumes. Higher precision with low relative standard deviation (RSD) were observed as the injection volume and concentration increased. In the injection of 0.5 ng/g, relatively higher RSD were observed owing to sensitivity problem and only 10 µl injections were generally satisfied the RSD value under 10. Most of peak area increased as much as injection volume increased, but not at the same proportion in 10 uL injection. The peak area were increased by 2.5 times when the injection volume of 2 uL increased to 5 uL, whereas the peak area in 10 uL injection were not increased by 2 times than those of 5 uL injections. The results were likely due to ion suppression phenomenon caused by large amount of ions in ionization process (Stahnke et al., 2012). Although large injection volume is one of the effective approach to provide low detection limit, it could lead to frequent maintenance of LC-MS/MS like cleaning source unit. We selected the injection volume of 5 uL in order to eliminate possibility of poor linearity in calibration curve as well as avoid carry-over problem that was previously discussed (Charalampous et al., 2015; Hughes et al., 2007).

Figure 18. Relative peak area of the methanol-based mobile phase (A) compared with acetonitrile-based mobile phase (B) at solvent standard mixture of 100 ng/g (n = 5, 100 ng/g). The graph were plotted against the number of pesticides ranked by relative peak area of (A).

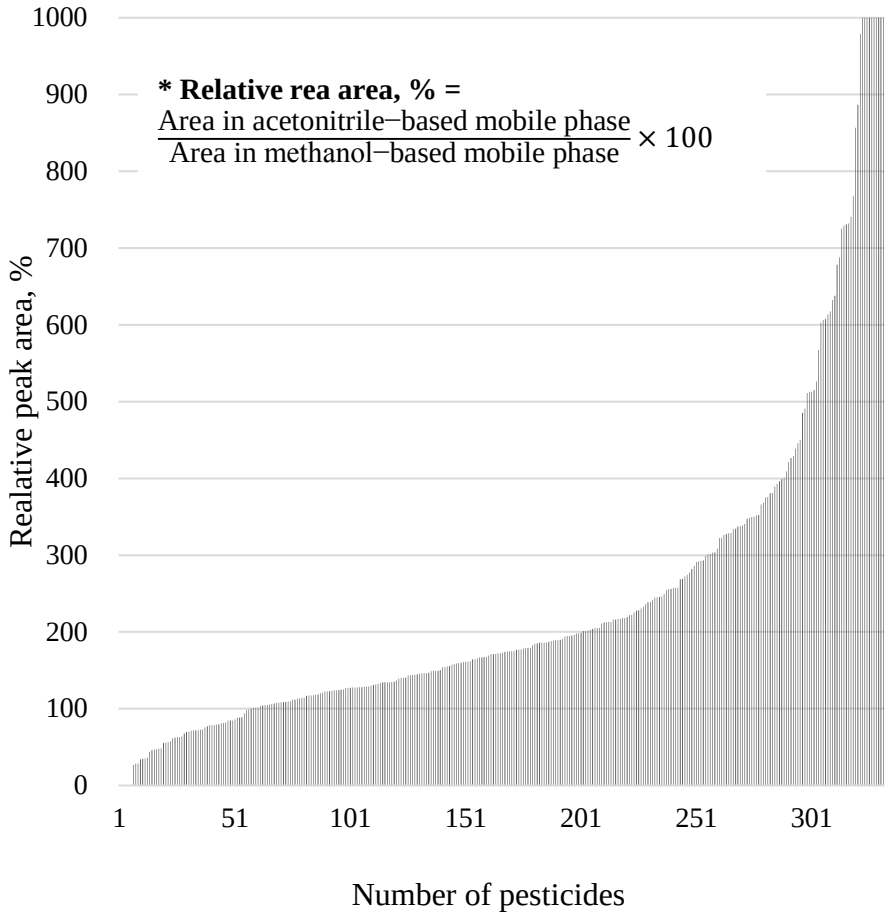
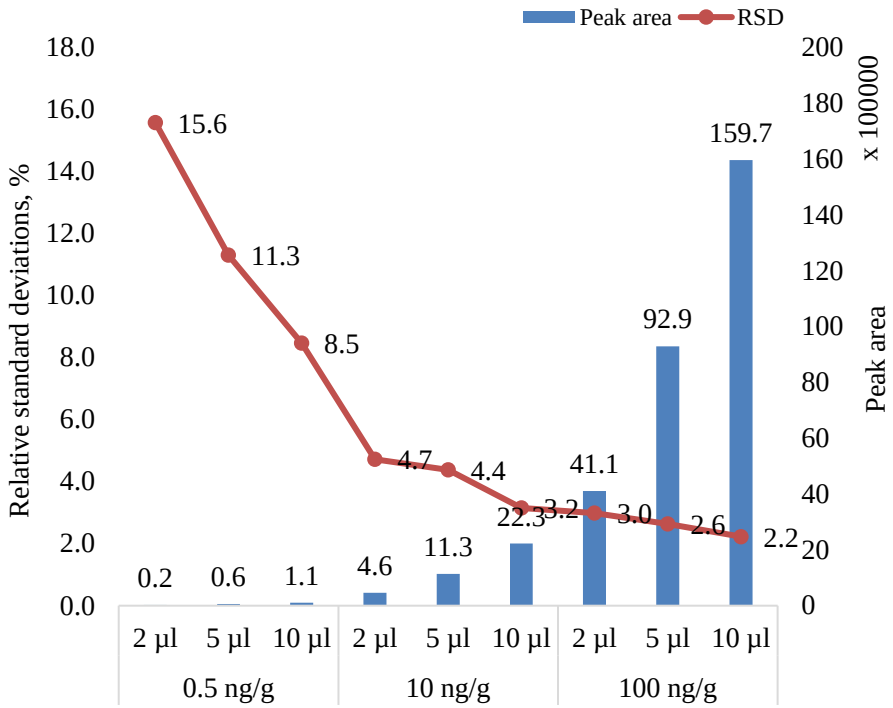

1000
900
800
700
600
500
400
300
200
100
0
Realative peak area, %
* Relative rea area, % =
Area in acetonitrile−based mobile phase / Area in methanol−based mobile phase × 100
1
51
101
151
201
251
301
Number of pesticides

Figure 19. Peak area and repeatability by injection volume (*n* = 5).


Peak area
RSD
Relative standard deviations, %
Peak area
x 100000
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
200
180
160
140
120
100
80
60
40
20
0
15.6
11.3
8.5
4.7
4.4
3.2
3.0
2.6
2.2
0.2
0.6
1.1
4.6
11.3
22.3
41.1
92.9
159.7
2 µl
5 µl
10 µl
2 µl
5 µl
10 µl
2 µl
5 µl
10 µl
0.5 ng/g
10 ng/g
100 ng/g

Optimization of cleanup procedure

In QuEChERS methodologies as well as other multiresidue analysis methods, pigments rich commodities such as leafy vegetables, carrots, and berries are challenging due to the coloured residues existed even after cleanup procedure. Among them, a green matrix containing high chlorophyll like a spinach in this study could give rise to chromatographic problem. The additional absorbents like GCB has been used for the purpose of the removal of chlorophyll, but it also known to retain planar structured pesticides (Anastassiades, Lehotay, et al., 2003; Hayward et al., 2015; Koesukwiwat et al., 2010; Mol et al., 2007). Although the previous studies have shown that the coextractives from chlorophyll-rich matrix did not affect quantitative results and chromatograms in GC-MS analysis (Lee et al., 2017; Lehotay, Maštovská, et al., 2005), there were not many studies about the effect on LC analysis. To check the necessity to eliminate the chlorophyll-coextractives and whether remained green matrix would affect to LC-MS/MS-amenable compounds, preliminary recovery test was performed by different amounts (2.5 and 7.5 mg) of GCB on spinach extracts.

Table 10 shows recoveries of representative pesticides in different dSPE absorbents. The pesticides were chosen on the basis of the reduced recovery rate as the amounts of GCB sorbents increased. The well-known pesticides for planar structured such as carbendazim, thiabendazole, and cyprodinil were decreased by addition of GCB, consistent with previous findings (Mol et al., 2007; Nie, Shui Miao, et al., 2015; Walorczyk, 2008; Wong et al., 2010). The pesticides containing aromatic moiety including phenylureas (forchlorfenuron and Thidiazuron) and benzoylureas (diflubenzuron and teflubenzuron) were also adsorbed on GCB. In addition, it was noticeable that the best result was obtained in PSA cleanup without GCB in terms of the frequency satisfying the

recoveries between of 70-120% with RSD $\leq$ 20%. No great difference in the frequency was observed compared with additional 2.5 mg of GCB, but the average recoveries was more close to 100% in PSA-only cleanup. Because there were also no effect on chromatographic separations or peak shapes, therefore, the dSPE containing PSA and $MgSO_4$ was chosen as cleanup procedure for method validation study.

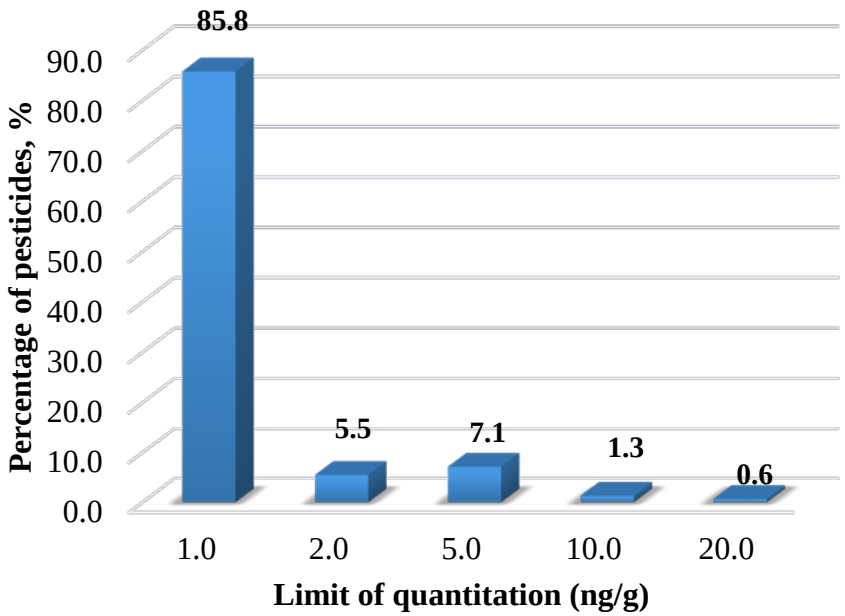
Table 10. Recoveries of representative pesticides from the cleanup with different types of dSPE sorbents in spinach (100 ng/g spiking level, *n = 3*).

Pesticides	Recovery (RSD) %		
	PSA only	PSA + GCB 2.5 mg	PSA + GCB 7.5 mg
Ametoctradin	90.5 (2.1)	85.7 (2.4)	68.3 (7.7)
Carbendazim	88.5 (1.5)	84.3 (1.5)	62.4 (9.7)
Clofentezine	92.3 (1.1)	93.4 (3.1)	67.1 (7.1)
Clomeprop	94.8 (4.5)	89.9 (1.7)	60.4 (14)
Cyprodinil	101.0 (1)	84.3 (4.8)	47.7 (14.3)
Diflubenzuron	93.7 (6.9)	92.1 (3.4)	75.7 (9.6)
Forchlorfenuron	87.2 (3.1)	73.4 (2.7)	27.8 (28.9)
Imibenconazole	91.9 (4.1)	86.2 (1)	54.4 (16.4)
Inabenfide	89.7 (3.8)	85.2 (11.7)	35.5 (35.5)
Mepanipyrim	94.2 (3.1)	83.7 (4)	56.2 (14.7)
Pymetrozine	92.2 (1.2)	98.6 (2.4)	89.8 (3.7)
Pyrimidifen	92.8 (7.8)	84.7 (6)	45.9 (27.4)
Teflubenzuron	104.2 (5.5)	93.7 (2.5)	64.3 (14.3)
Thiabendazole	86.8 (1.4)	80.1 (3.2)	45.0 (12.3)
Thidiazuron	86.5 (3.2)	70.6 (3)	22.5 (30.5)
The pesticides satisfying recovery of 70-120% with RSD ≤ 20%	**Number of pesticides (percentage, %)**		
	282 (91.0)	**281 (90.6)**	**262 (84.5)**

Method validation

Recovery test was carried out to validate the analytical method by spiking 332 pesticides into three blank samples (brown rice, orange, and spinach) at fortification levels of 10 and 50 ng/g ($n = 5$). The calibrations curves for quantitation were obtained by matrix-matched calibration from each sample matrices. The correlation coefficient (r^2) were obtained from the calibration curves of each commodities in each recovery test. High levels of linearity (r^2), with ≥ 0.99 were achieved in most of compounds, ranging from 1 to 100 ng/g. (**Table S5**). When the LOQs were defined as the minimum concentrations having an S/N $\geq$ 10, the 85.8% (265 compounds) of pesticides had 1 ng/g of LOQs (**Figure 20**). In most case the LOQs were satisfied less than or equal to the 10 ng/g. But two pesticides (atrazine and inabenfide) had 20 ng/g of LOQ due to the low sensitivity.

Figure 20. Distribution of limit of quantitation in LC-MS/MS analysis.


85.8
5.5
7.1
1.3
0.6
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Percentage of pesticides, %
1.0
2.0
5.0
10.0
20.0
Limit of quantitation (ng/g)

The results of recovery tests were evaluated according to acceptability criteria of DG-SANTE guidelines (Hanot et al., 2015). The recoveries in three commodities are summarized in **Figure 21**. In the low spiking level (10 ng/g), 86.8–88.7% of pesticides met the validation criteria with recoveries in the range of 70–120% and RSD $\leq$ 20%. Slightly better satisfactory frequencies (91.9–96.1%) were obtained in the high spiking level (10 ng/g), owing to improved recoveries of several pesticides having low signal intensity. There were no significantly differences between different in the types of matrices while the good and excellent recovery results were achieved.

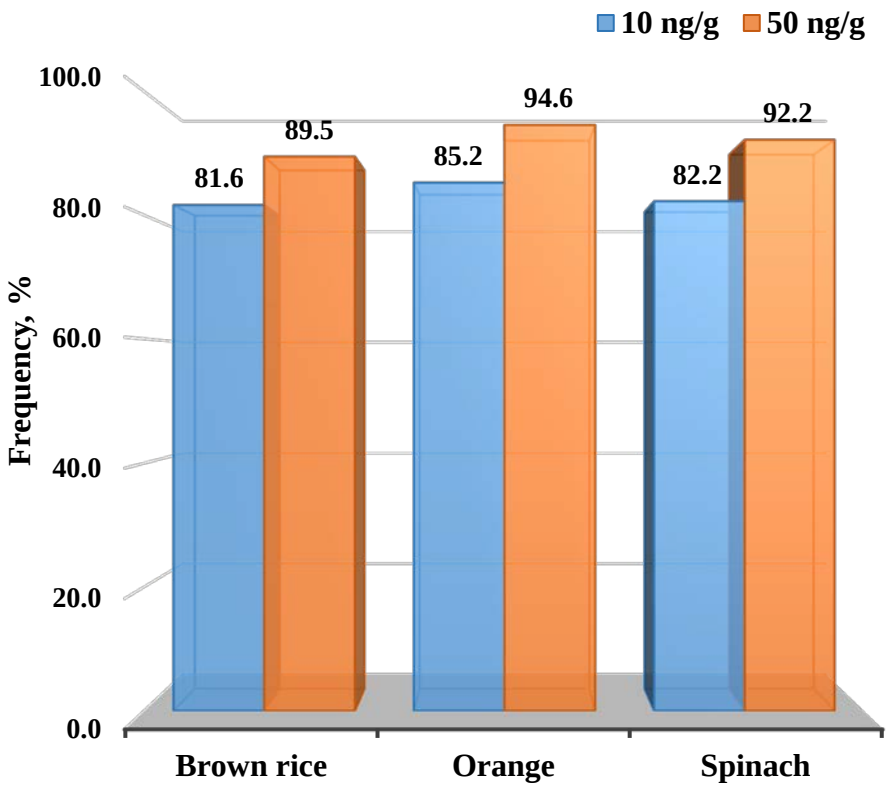
On the other hand, the sulfonylurea pesticides including bensulfuron-methyl, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, thifensulfuron-methyl, and tribenuron-methyl gave poor recoveries. The results were consistent with previous studies, in which sulfonylurea pesticides showed undesirable recoveries using QuEChERS methods. This could be explained by the acidic properties of sulfonylurea pesticides, which can be easily adsorbed by PSA. To increase the recoveries of the sulfonylurea pesticides, Kaczyński and Łozowicka (2017) added chitin for the purpose of purification with citrate buffered QuEChERS, skipping the PSA cleanup procedure.

The imidazolinone pesticides (imazamox, imazapic, imazaquin, and imazethapyr), one of the acidic pesticides, were showed low recoveries (< 20%) with high RSDs. Jadhav et al. (2015) previously reported that the ethyl acetate extraction with control of pH or citrate buffered QueChERS without PSA cleanup helped to increase the recoveries of acidic pesticides such as imazethapyr and imazosulfuron. Because these pesticides are stabilized to non-ionised form in acidic condition resulting in remaining in the organic layer in the extraction step. The cleanup utilized combination of Z-Sep+ with PSA after acetate buffered extraction has been used to enhance the recovery (Kiljanek et

al., 2016).

Interestingly, about 200% of methomyl recoveries were observed at brown rice while thiodicarb were almost disappeared with not-detectable residue. This results was assumed to be due to the unstable property of thiodicarb converting into methomyl (Jones et al., 1989; Wu et al., 2013). Since the good results were observed in the orange and spinach without any enhanced or decreased recoveries, it is noteworthy that grains may help hydrolysis of thiodicarb into methomyl. For other compounds, many polar pesticides (e.g., asulam, cyromazine, haloxyfop, mecoprop-P, and penoxsulam) also showed poor recoveries in this study. The alternative methods like the QuPPe-Method (Anastassiades et al., 2016) by acidified methanolic extraction skipping the PSA cleanup thought to be helpful to improve the recovery of polar pesticides. Details of the recovery results including LOQ and linearity (r^2) data in all of the tests can be found in Table S5.

Figure 21. Percentages of pesticides satisfying the recovery rates of 70-120% and RSD≤20% at 0.01 and 0.05 mg/kg spike levels, using the optimized method in this study.


10 ng/g
50 ng/g
100.0
80.0
60.0
40.0
20.0
0.0
Frequency, %
81.6
89.5
85.2
94.6
82.2
92.2
Brown rice
Orange
Spinach

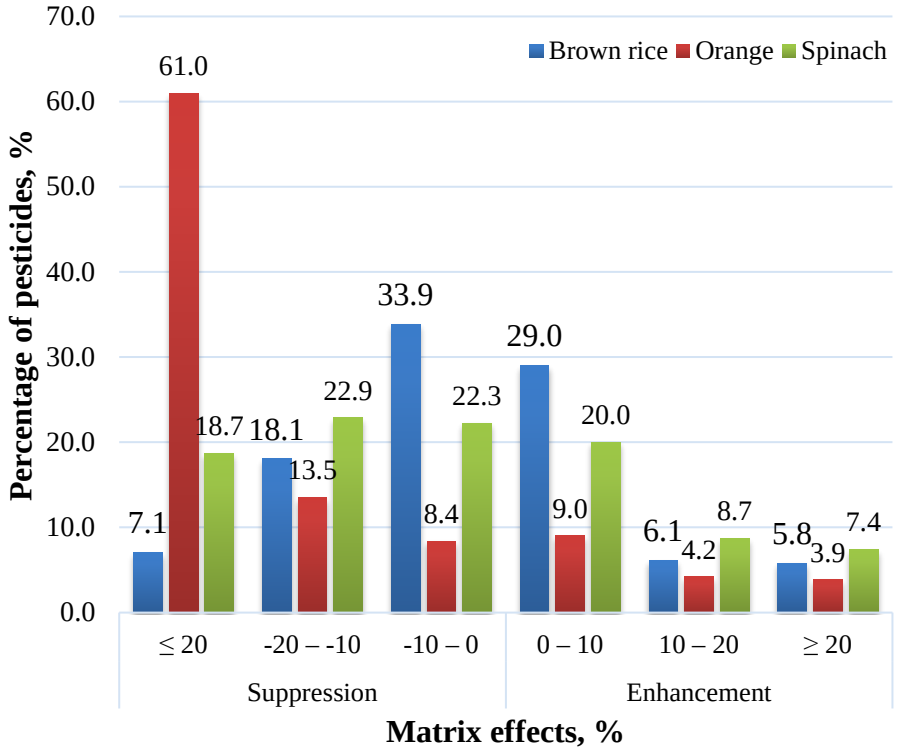
Matrix effects

The peak response obtained from LC-MS/MS may be affected by co-elution of matrix components. Recent sample preparation methods prior to instrumental analysis tend to eliminate the minimum matrix interferences as possible in order to reduce the loss of recovery of target compounds. Consequently, the presence of matrix co-extracts leads to increase the possibility of matrix effect and inaccurate quantitation. The compensation method by matrix-matched calibration has been a widely used alternative way to overcome matrix effect. It should be noted that it is difficult to prepare the exactly same matrix with the target sample even though it is same kinds of commodities in routine analysis. Therefore, it is important to understand the tendency of matrix effect in each compound.

The matrix effects were determined by comparing the peak area between solvent-only standard and matrix matched standards (brown rice, orange, and spinach). According to the equation mentioned in the method section, a positive value of ME indicates signal enhancement, whereas a negative value indicates signal suppression. **Figure 22** shows the distribution of MEs in three matrices. The matrix effects were evenly spread across the each range. In the case of brown rice and spinach, 87.4 and 74.1% of pesticides showed soft matrix effect (< ±20%) (He, Chen, et al., 2015), which is acceptability criteria according to SANTE guideline (European Commission, 2015). However, high percentage of pesticide (61%) in orange was calculated under -20% of matrix effect, indicating significant matrix-induced suppression. Although the degree of matrix effect was not much higher than those of GC-MS/MS results (Lee et al., 2017; Lozano et al., 2014), more matrix-dependent results were obtained. Matrix effects in LC–MS/MS cause because of co-eluting interference interacting with the pesticides in the electrospray ionization

process, producing suppression or enhancement of the signal compared to the signal of the analyte injected in solvent (Lozano, Kiedrowska, Scholten, de Kroon, de Kok and Fernández-Alba, 2016). As it also described in the literature (European Commission, 2015; Niell et al., 2014), this can be explained that matrix effect in LC-MS/MS, unlike in GC-MS/MS, depends on co-elution of target analyte with coextracts that could be vary between different commodities. These results identified again the necessity of matrix-matched calibration using the equivalent matrix as possible for proper quantitation of compounds.

Figure 22. Graphical comparison of the absolute values of matrix effects (ME) results.


70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Percentage of pesticides, %
Brown rice
Orange
Spinach
61.0
18.7
18.1
13.5
22.9
33.9
8.4
22.3
29.0
9.0
20.0
6.1
4.2
8.7
5.8
3.9
7.4
≤ 20
-20 – -10
-10 – 0
0 – 10
10 – 20
≥ 20
Suppression
Enhancement
Matrix effects, %

Real sample analysis

It should be noted that the Korean Ministry of Food and Drug Safety is now prepared for introducing a positive list system for the most protective regulation of pesticide residues on all the agricultural produce or commodities coming 2018 to keep up with the current worldwide trend. In the case of tropical fruits, it has already begun to apply. Unlike the traditional system, the new system would not allow the pesticides (with ≥ 0.01 mg/kg level) which are not registered or does not have maximum residue limit (MRL) for a specific item. The optimized method was applied to real sample analysis to prove the effectiveness. The apple, easily purchasable, which is one of the most frequently consumed fruits was selected for real sample analysis. In addition, it was also considered that the different commodity is more suitable to check the possibility to apply in routine analysis. A total of 16 inorganic apple samples were collected from different markets. The certificated organic apple sample was used for quality control and matrix-matched calibration. For quality control on apple analysis, pesticides mixture containing 332 pesticides was spiked at concentration of 20 ng/g ($n = 3$). The detected pesticides and QC results of each pesticides are shown **Table 11**. A total of 19 pesticides were detected and most of them are insecticides except for four fungicides. On the whole, all samples contained one or more pesticide residues. Except for one sample contained only one pesticide, all of the samples had 4-10 kinds of pesticide multiresidues. Out of the 16 samples, none of the pesticides were detected above the maximum residue limit (MRL) of Korea (Korean Pesticides MRLs in Food; 2016;, 2016). Most frequently found pesticides were etofenprox (87.5%), carbendazim (81.3%), and tebuconazole (75.0%) in detected samples but, with low residue

levels compared with its MRLs. Meanwhile, thiophanate-methyl, which is known to degrade into carbendazim in the environment (Fan et al., 2013), was not detected in any samples. It was reported that as soon as thiophanate-methyl was applied to plant, converted into carbendazim, providing fungicidal activity (Buchenauer et al., 1973; Cycoń et al., 2011).

Table 11. Results of real sample analysis by LC-MS/MS in a total of 16 apple samples. The detected pesticides were summarized with maximum residue limit in Korea and QC results of each pesticides.

No.	Pesticide	QC results (Rec. ± RSD, %)[a]	No. of detections	Detection frequency, %	Min. conc. (ng/g)	Max. conc. (ng/g)	MRL[b] in Korea (ng/g)
1	Acetamiprid	96.4 ± 11.0	2	12.5	17.6	91.1	300
2	Buprofezin	86.1 ± 15.0	1	6.3	124.9	124.9	500
3	Carbendazim	86.6 ± 2.2	13	81.3	2.6	863.9	3000
4	Chlorantraniliprole	99.5 ± 0.9	2	12.5	22.8	27.0	1000
5	Chlorfluazuron	101.3 ± 3.9	2	12.5	12.5	39.8	200
6	Chlorpyrifos	95.8 ± 8.2	7	43.8	1.8	14.4	1000
7	Deltamethrin	112.4 ± 10.1	10	62.5	6.4	26.7	500
8	Difenoconazole	86.1 ± 1.3	10	62.5	4.8	41.0	1000
9	Diflubenzuron	87.8 ± 6.0	6	37.5	23.5	502.6	2000
10	Dinotefuran	77.0 ± 8.0	4	25.0	1.9	49.4	500
11	Etofenprox	95.7 ± 8.5	14	87.5	9.6	229.5	1000
12	Fenpropathrin	114.6 ± 12.0	1	6.3	34.4	34.4	5000
13	Fluquinconazole	91.3 ± 5.5	1	6.3	61.4	61.4	500
14	Metconazole	81.5 ± 2.8	6	37.5	17.1	153.3	1000
15	Novaluron	73.1 ± 15.3	6	37.5	7.5	78.4	1000
16	Pyraclostrobin	74.8 ± 6.3	8	50.0	4.8	71.8	200
17	Tebuconazole	76.7 ± 6.6	12	75.0	7.5	283.3	500
18	Teflubenzuron	93.3 ± 5.4	2	12.5	12.1	104.2	1000
19	Trifloxystrobin	79.3 ± 2.5	3	18.8	18.2	151.6	700

Notes: [a]Average recovery (Rec.) and relative standard deviation (RSD) at 20 ng/g ($n = 3$). [b]Maximum residue limit on apple

Conclusion

This research presented a rapid and efficient simultaneous multiresidue method for 500 pesticides by GC-MS/MS and LC-MS/MS in food matrices. Multiple reaction monitoring parameters such as quantifier ion, qualifier ion, and collision energy were carefully optimized to obtain high selectivity and sensitivity, resulting in a final screen of 360 pesticides by GC-MS/MS and 332 pesticides by LC-MS/MS. To make the GC-MS/MS technique more practical for routine multiresidual analysis, short and microbore column (20 m length, 0.18 mm i.d.), priming injection, pressure pulse injection (PPI), and automated adjustment of retention time function (AART) were employed, giving improvement of peak sensitivity and shorter analytical time (within 20 min).

The modified QuEChERS (0.1 % formic acid in acetonitrile) extraction gave fewer co-extracts in the final extract and higher acceptable recovery results than other QuEchERS approaches. The dSPE cleanup with additional sorbents (GCB and ChloroFiltr) decreased the recovery of some pesticides having planar and aroma moiety, remained chlorophyll in final extracts did not cause an adverse effect on chromatographic and quantitation results. Final optimized method was successfully validated in terms of accuracy, precision, selectivity, and sensitivity. The applicability of some pesticides, which has not been studied was also evaluated from the validation study. Finally, the developed methodology was applied to the analysis of real samples for testing the applicability of the method.

Supplementary Information

Table S1. The optimized GC-MS/MS parameters including retention time of each pesticide, SRM transitions, and collision energies

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
1	2,6-Diisopropylnaphthalene	7.56	212.0>197.2 (12)	212.0>155.1 (24)
2	Acetochlor	8.34	174.0>146.1 (12)	223.0>132.1 (18)
3	Acibenzolar-S-methyl	8.58	135.0>63.1 (24)	182.0>135.0 (18)
4	Acrinathrin	13.38	289.0>93.1 (15)	289.0>77.2 (30)
5	Alachlor	8.45	188.0>160.1 (9)	188.0>131.1 (21)
6	Aldrin	9.02	263.0>190.9 (30)	263.0>192.9 (30)
7	Allidochlor	5.25	132.0>56.1 (9)	132.0>77.0 (15)
8	Ametoctradin	13.60	246.0>188.2 (27)	246.0>174.1 (30)
9	Ametryn	8.54	227.0>170.0 (15)	212.0>122.1 (12)
10	Anilofos	12.59	226.0>157.0 (15)	184.0>157.0 (9)
11	Atrazine	7.63	215.0>58.1 (12)	20.0>122.1 (9)
12	Azaconazole	10.51	217.0>173.0 (15)	173.0>109.1 (27)
13	Azinphos-ethyl	13.50	160.0>132.1 (6)	160.0>77.1 (21)
14	Azinphos-methyl	12.96	160.0>77.1 (18)	132.0>77.1 (15)
15	Azoxystrobin	16.49	344.0>172.1 (30)	344.0>156.1 (30)
16	Benalaxyl	11.32	234.0>146.2 (21)	266.0>148.2 (9)
17	Bendiocarb	7.22	166.0>151.1 (15)	126.0>52.1 (18)
18	Benfuresate	8.27	163.0>121.1 (9)	256.0>163.1 (9)
19	Benodanil	11.13	231.0>202.9 (18)	323.0>230.8 (21)
20	Benthiavalicarb-isopropyl	13.01	158.0>116.1 (6)	158.0>72.1 (12)
21	Benzoylprop-ethyl	12.05	292.0>105.1 (15)	260.0>186.0 (18)
22	BHC, α-	7.43	181.0>145.0 (15)	219.0>183.0 (9)
23	BHC, β-	7.76	181.0>145.0 (18)	219.0>183.0 (9)
24	BHC, δ-	8.05	181.0>145.0 (15)	219.0>183.0 (9)
25	BHC, γ-	7.68	181.0>145.0 (15)	219.0>183.0 (12)
26	Bifenazate	12.41	258.0>199.1 (12)	196.0>141.1 (21)
27	Bifenox	12.61	341.0>310.0 (9)	310.0>189.0 (9)
28	Bifenthrin	12.31	166.0>164.1 (30)	181.0>141.1 (21)
29	Binapacryl	10.54	83.0>55.0 (9)	83.0>53.0 (15)
30	Bitertanol	13.89	170.0>141.1 (24)	170.0>115.1 (30)
31	Bixafen	15.16	159.0>139.0 (15)	413.0>159.1 (15)
32	Boscalid	14.83	342.0>140.0 (15)	342.0>112.1 (30)
33	Bromacil	8.86	205.0>188.0 (15)	207.0>163.9 (18)
34	Bromobutide	8.37	232.0>176.2 (9)	232.0>114.1 (9)
35	Bromophos	9.22	331.0>93.1 (30)	329.0>93.0 (27)
36	Bromopropylate	12.36	341.0>183.0 (21)	183.0>76.1 (27)
37	Bupirimate	10.42	273.0>108.0 (15)	208.0>165.1 (15)
38	Buprofezin	10.42	172.0>57.1 (15)	172.0>131.1 (6)
39	Butachlor	9.91	176.0>147.1 (15)	237.0>160.2 (15)
40	Butafenacil	14.26	331.0>180.0 (21)	331.0>152.1 (30)
41	Butralin	9.15	266.0>174.1 (21)	224.0>132.1 (18)
42	Butylate	6.03	156.0>57.1 (15)	146.0>90.0 (9)
43	Cadusafos	7.31	159.0>97.0 (18)	213.0>89.1 (15)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
44	Cafenstrole	14.37	10.0>72.1 (6)	188.0>119.1 (21)
45	Captafol	12.20	79.0>77.1 (15)	79.0>51.0 (24)
46	Captan	9.65	149.0>79.1 (18)	149.0>105.1 (6)
47	Carbaryl	8.53	144.0>115.1 (24)	115.0>89.1 (18)
48	Carbofuran	7.56	164.0>149.1 (12)	164.0>103.1 (24)
49	Carbophenothion	11.36	342.0>157.1 (15)	342.0>199.1 (6)
50	Carbosulfan	12.17	118.0>76.0 (6)	160.0>57.1 (15)
51	Carboxin	10.47	235.0>143.0 (9)	235.0>87.0 (21)
52	Chinomethionat	9.88	234.0>205.9 (12)	206.0>148.1 (15)
53	Chlordane-*cis*	10.03	377.0>267.9 (27)	377.0>266.0 (24)
54	Chlordane-*trans*	9.85	377.0>266.0 (24)	377.0>267.9 (27)
55	Chlorethoxyfos	6.97	153.0>97.0 (12)	153.0>125.0 (6)
56	Chlorfenapyr	10.55	247.0>227.2 (15)	247.0>20.0 (27)
57	Chlorfenson	10.17	175.0>111.0 (9)	302.0>175.0 (9)
58	Chlorfenvinphos	9.49	267.0>159.0 (18)	323.0>266.9 (18)
59	Chlorfluazuron	7.17	171.0>127.0 (15)	213.0>171.1 (9)
60	Chlorflurenol-methyl	9.74	274.0>215.0 (18)	215.0>180.1 (18)
61	Chlorobenzilate and chloropropylate	10.81	139.0>75.1 (27)	251.0>111.1 (27)
62	Chloroneb	6.43	191.0>113.0 (15)	191.0>141.0 (9)
63	Chlorothalonil	7.94	264.0>168.0 (27)	266.0>168.0 (24)
64	Chlorpropham	7.17	127.0>65.1 (21)	213.0>171.0 (9)
65	Chlorpyrifos	8.93	314.0>257.8 (18)	258.0>166.0 (24)
66	Chlorpyrifos-methyl	8.37	286.0>93.1 (24)	286.0>270.9 (18)
67	Chlorthal-dimethyl	9.00	301.0>222.8 (24)	332.0>30.70 (18)
68-1	Chlorthiophos-1	10.79	325.0>268.9 (15)	269.0>204.9 (18)
68-2	Chlorthiophos-2	10.98	325.0>268.9 (15)	269.0>204.9 (18)
69	Chlozolinate	9.45	188.0>147.0 (18)	259.0>188.0 (15)
70	Cinmethylin	8.56	105.0>77.0 (18)	123.0>81.1 (9)
71	Clomazone	7.68	204.0>107.1 (21)	125.0>99.0 (18)
72	Clomeprop	12.70	288.0>120.2 (24)	288.0>169.0 (18)
73	Coumaphos	14.07	362.0>109.1 (18)	362.0>226.0 (15)
74	Cyanazine	8.95	225.0>189.1 (15)	198.0>91.1 (9)
75	Cyanophos	7.77	243.0>109.0 (15)	125.0>79.0 (9)
76	Cycloate	7.08	154.0>83.1 (9)	154.0>55.1 (21)
77	Cyflufenamid	10.55	412.0>118.0 (24)	412.0>90.0 (30)
78	Cyflumetofen	12.81	173.0>145.0 (15)	173.0>95.1 (30)
79-1	Cyfluthrin-1	14.47	163.0>127.0 (6)	226.0>206.1 (15)
79-2	Cyfluthrin-2	14.57	163.0>127.0 (6)	226.0>206.0 (15)
79-3	Cyfluthrin-3	14.62	163.0>127.0 (6)	226.0>206.1 (15)
79-4	Cyfluthrin-4	14.66	163.0>127.0 (6)	226.0>206.1 (15)
80	Cyhalofop-butyl	13.08	256.0>120.1 (12)	229.0>109.1 (15)
81-1	Cyhalothrin-1	13.04	197.0>141.1 (12)	197.0>161.1 (6)
81-2	Cyhalothrin-2	13.21	197.0>141.1 (12)	197.0>161.1 (6)
82-1	Cypermethrin-1	14.77	163.0>127.1 (9)	163.0>109.0 (24)
82-2	Cypermethrin-2	14.88	163.0>127.1 (9)	163.0>109.0 (24)
82-3	Cypermethrin-3	14.97	163.0>127.1 (9)	163.0>109.0 (24)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
82-4	Cypermethrin-4	14.97	163.0>127.1 (9)	163.0>109.0 (24)
83	Cyproconazole	10.67	222.0>125.0 (24)	139.0>75.1 (27)
84	Cyprodinil	9.40	224.0>208.1 (21)	225.0>210.1 (18)
85	DDD, *o*, *p*'-	10.43	235.0>165.1 (24)	165.0>163.1 (30)
86	DDD, *p*, *p*'-	10.96	235.0>165.1 (24)	235.0>199.0 (18)
87	DDE, *o*, *p*'-	9.86	246.0>176.1 (30)	318.0>245.9 (27)
88	DDE, *p*, *p*'-	10.33	246.0>176.1 (27)	318.0>246.0 (21)
89	DDT, *o*, *p*'-	11.00	235.0>165.1 (24)	235.0>199.1 (18)
90	DDT, *p*, *p*'-	11.55	235.0>165.1 (24)	235.0>199.0 (18)
91	Deltamethrin	16.33	253.0>172.0 (9)	253.0>174.0 (9)
92	Desmetryn	8.30	213.0>171.1 (9)	198.0>108.1 (15)
93-1	Di-Allate-1	7.35	234.0>150.0 (21)	234.0>192.0 (12)
93-2	Di-Allate-2	7.44	234.0>150.0 (21)	234.0>192.1 (15)
94	Diazinon	7.81	137.0>84.1 (15)	304.0>179.2 (15)
95	Dichlobenil	5.58	171.0>10.1 (27)	136.0>10.0 (9)
96	Dichlofenthion	8.29	279.0>222.9 (18)	251.0>223.0 (9)
97	Dichlofluanid	8.83	224.0>123.1 (15)	224.0>77.1 (30)
98	Dichlormid	5.63	172.0>108.1 (9)	166.0>56.1 (9)
99	Dichlorvos	5.00	185.0>93.0 (15)	220.0>185.0 (6)
100	Diclofop-methyl	11.77	253.0>162.1 (21)	340.0>253.0 (18)
101	Dicloran	7.55	206.0>176.0 (12)	206.0>124.1 (27)
102	Dicofol	9.14	139.0>111.1 (15)	250.0>139.1 (15)
103	Dicrotophos	7.19	127.0>95.0 (18)	193.0>127.0 (6)
104	Dieldrin	10.43	279.0>206.9 (27)	263.0>192.9 (30)
105	Diethatyl-ethyl	10.02	262.0>188.2 (12)	262.0>160.2 (21)
106	Diethofencarb	8.92	196.0>168.1 (6)	225.0>96.1 (27)
107-1	Difenoconazole-1	16.04	323.0>265.0 (18)	265.0>202.1 (18)
107-2	Difenoconazole-2	16.10	323.0>265.0 (18)	265.0>202.1 (18)
108	Diflufenican	11.80	394.0>266.0 (21)	266.0>246.1 (15)
109	Dimepiperate	9.64	145.0>112.1 (9)	145.0>69.1 (18)
110	Dimethachlor	8.30	134.0>105.1 (15)	197.0>148.1 (12)
111	Dimethametryn	9.45	212.0>122.1 (12)	212.0>94.1 (21)
112	Dimethenamid	8.31	230.0>154.1 (12)	154.0>111.1 (15)
113	Dimethipin	7.64	118.0>58.0 (9)	118.0>90.1 (3)
114	Dimethoate	7.53	229.0>87.1 (12)	87.0>72.0 (24)
115-1	Dimethomorph-1	16.60	301.0>165.1 (12)	387.0>301.1 (15)
115-2	Dimethomorph-2	16.89	301.0>165.1 (12)	387.0>301.1 (15)
116	Dimethylvinphos	8.95	295.0>109.1 (18)	295.0>79.1 (30)
117	Diniconazole	10.91	268.0>232.1 (12)	268.0>149.1 (27)
118	Dinitramine	7.92	261.0>241.1 (9)	261.0>195.1 (21)
119	Dioxathion	7.72	270.0>197.1 (6)	270.0>141.0 (18)
120	Diphenamid	9.22	167.0>165.1 (24)	239.0>167.1 (6)
121	Diphenylamine	7.04	169.0>167.1 (27)	168.0>166.2 (30)
122	Disulfoton	7.95	142.0>109.0 (6)	186.0>153.1 (6)
123	Dithiopyr	8.57	354.0>306.0 (9)	306.0>286.0 (9)
124	Edifenphos	11.42	173.0>109.0 (15)	310.0>173.0 (15)
125	Endosulfan, *α*-	10.04	241.0>205.9 (15)	339.0>160.0 (21)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
126	Endosulfan, *β*-	10.90	339.0>160.0 (18)	339.0>267.0 (9)
127	Endosulfan, sulfate-	11.46	272.0>236.8 (18)	272.0>234.70 (15)
128	Endrin	10.74	345.0>281.0 (9)	317.0>209.0 (30)
129	EPN	12.33	169.0>77.1 (24)	157.0>110.0 (15)
130	Epoxiconazole	11.99	192.0>138.0 (15)	192.0>111.0 (27)
131	EPTC	5.64	189.0>128.2 (6)	189.0>86.1 (12)
132	Esprocarb	8.83	222.0>91.1 (15)	162.0>91.1 (9)
133-1	Etaconazole-1	10.88	173.0>109.0 (27)	245.0>55.0 (15)
133-2	Etaconazole-2	10.94	173.0>109.0 (27)	245.0>55.0 (15)
134	Ethalfluralin	7.10	276.0>202.0 (15)	316.0>276.0 (12)
135	Ethiofencarb	8.20	107.0>77.1 (18)	168.0>107.1 (15)
136	Ethion	10.93	231.0>128.9 (27)	231.0>174.9 (12)
137	Ethofumesate	8.74	207.0>137.1 (12)	207.0>179.1 (6)
138	Ethoprophos	7.06	20.0>158.0 (6)	158.0>97.0 (15)
139	Ethoxyquin	7.55	202.0>174.1 (15)	174.0>131.1 (18)
140	Etofenprox	15.08	163.0>135.1 (9)	163.0>107.1 (18)
141	Etoxazole	12.45	30.0>270.30 (27)	330.0>57.1 (21)
142	Etridiazole	6.16	211.0>182.9 (12)	183.0>139.9 (15)
143	Etrimfos	7.99	292.0>181.2 (9)	292.0>153.1 (21)
144	Fenamidone	12.50	268.0>180.1 (21)	238.0>103.1 (30)
145	Fenamiphos	10.15	303.0>195.2 (9)	288.0>260.1 (6)
146	Fenarimol	13.39	219.0>107.1 (15)	251.0>139.0 (15)
147	Fenazaquin	12.64	160.0>145.1 (9)	160.0>117.1 (24)
148	Fenbuconazole	14.44	198.0>129.1 (9)	129.0>102.1 (15)
149	Fenchlorphos	8.57	285.0>269.9 (15)	287.0>271.9 (18)
150	Fenclorim	7.42	224.0>189.0 (15)	189.0>104.1 (15)
151	Fenfuram	8.01	201.0>109.1 (12)	109.0>53.0 (15)
152	Fenhexamid	11.56	177.0>113.0 (15)	301.0>97.2 (15)
153	Fenitrothion	8.73	277.0>260.0 (6)	260.0>125.0 (15)
154	Fenobucarb	6.92	121.0>77.1 (21)	150.0>121.1 (9)
155	Fenothiocarb	9.93	160.0>72.1 (15)	160.0>55.1 (18)
156	Fenoxanil	10.67	189.0>125.0 (15)	293.0>155.1 (24)
157	Fenpiclonil	12.17	236.0>174.1 (24)	201.0>166.1 (15)
158	Fenpropathrin	12.48	265.0>210.1 (15)	181.0>127.1 (27)
159	Fenpyrazamine	13.41	230.0>132.2 (15)	230.0>115.1 (24)
160	Fenson	9.21	141.0>77.1 (15)	268.0>141.0 (9)
161	Fensulfothion	10.85	293.0>97.0 (24)	293.0>125.0 (15)
162	Fenthion	8.98	278.0>109.0 (21)	278.0>169.0 (18)
163-1	Fenvalerate-1	15.62	225.0>119.1 (18)	419.0>167.1 (12)
163-2	Fenvalerate-2	15.82	225.0>119.1 (18)	419.0>167.1 (12)
164	Fipronil	9.41	367.0>213.0 (30)	369.0>214.9 (30)
165	Flonicamid	6.88	174.0>146.0 (15)	146.0>126.0 (9)
166	Fluacrypyrim	11.04	145.0>102.1 (24)	145.0>115.1 (15)
167	Fluazifop-butyl	10.66	282.0>91.1 (21)	254.0>146.0 (27)
168	Fluazinam	11.07	417.0>386.70 (18)	387.0>358.40 (21)
169	Fluchloralin	7.83	306.0>264.0 (9)	264.0>206.1 (9)
170-1	Flucythrinate-1	14.93	199.0>107.1 (27)	225.0>147.1 (12)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
170-2	Flucythrinate-2	15.13	199.0>107.1 (27)	225.0>147.1 (12)
171	Fludioxonil	10.23	248.0>127.1 (27)	248.0>154.1 (21)
172	Flufenacet	9.01	151.0>95.1 (27)	211.0>123.1 (12)
173	Flumetralin	9.89	143.0>107.1 (24)	143.0>83.1 (24)
174	Flumiclorac-pentyl	16.47	423.0>318.2 (12)	423.0>308.1 (15)
175	Flumioxazin	15.59	354.0>176.1 (24)	354.0>108.1 (21)
176	Fluopicolide	11.56	209.0>182.0 (15)	347.0>172.0 (27)
177	Fluopyram	9.50	173.0>145.1 (18)	223.0>196.0 (18)
178	Fluquinconazole	14.08	340.0>298.0 (18)	340.0>286.0 (27)
179	Flurochloridone	9.12	174.0>145.0 (27)	311.0>174.1 (24)
180	Flurtamone	12.78	333.0>120.1 (15)	199.0>157.1 (18)
181	Flusilazole	10.42	233.0>165.1 (18)	206.0>137.1 (18)
182	Fluthiacet-methyl	17.48	403.0>56.2 (24)	405.0>56.1 (21)
183	Flutianil	15.22	426.0>231.1 (15)	426.0>216.0 (30)
184	Flutolanil	10.13	323.0>173.1 (21)	323.0>281.2 (9)
185	Flutriafol	10.08	219.0>123.1 (15)	219.0>95.1 (30)
186-1	Fluvalinate-1	15.75	250.0>55.1 (21)	250.0>20.1 (21)
186-2	Fluvalinate-2	15.81	250.0>55.1 (18)	250.0>20.1 (18)
187	Folpet	9.71	260.0>130.1 (15)	260.0>231.9 (9)
188	Fonofos	7.83	246.0>137.0 (6)	246.0>109.0 (18)
189	Formothion	8.18	170.0>93.0 (9)	224.0>125.1 (21)
190-1	Fosthiazate-1	9.24	195.0>103.0 (9)	195.0>60.1 (21)
190-2	Fosthiazate-2	9.27	195.0>103.0 (9)	195.0>60.0 (18)
191	Furathiocarb	12.72	163.0>135.1 (6)	163.0>107.1 (15)
192	Halfenprox	14.83	265.0>117.1 (15)	265.0>115.1 (24)
193	Heptachlor	8.57	272.0>236.8 (18)	272.0>234.8 (18)
194	Heptachlor epoxide	9.52	353.0>262.8 (18)	353.0>281.9 (15)
195	Heptenophos	6.75	124.0>89.1 (15)	124.0>63.1 (27)
196	Hexachlorobenzene	7.47	284.0>248.8 (21)	286.0>213.8 (30)
197	Hexaconazole	10.20	214.0>159.0 (21)	256.0>159.0 (24)
198	Hexazinone	11.63	171.0>71.1 (18)	171.0>85.1 (15)
199	Hexythiazox	9.88	184.0>149.1 (6)	227.0>184.1 (6)
200	Imazalil	10.25	173.0>109.1 (27)	215.0>159.0 (9)
201	Imibenconazole	17.16	375.0>260.0 (21)	375.0>305.9 (12)
202	Indanofan	12.58	310.0>139.1 (6)	310.0>171.1 (12)
203	Indoxacarb	16.21	218.0>203.0 (12)	264.0>176.1 (15)
204	Ipconazole	13.31	125.0>89.1 (18)	125.0>99.0 (18)
205	Ipfencarbazone	13.79	198.0>156.1 (9)	229.0>159.0 (15)
206	Iprobenfos	8.11	204.0>91.1 (9)	204.0>121.1 (27)
207	Iprodione	12.18	314.0>244.9 (15)	316.0>56.1 (21)
208-1	Iprovalicarb-1	10.50	158.0>116.1 (6)	158.0>72.1 (12)
208-2	Iprovalicarb-2	10.50	158.0>116.1 (6)	158.0>72.1 (12)
209	Isazofos	7.95	257.0>162.1 (9)	257.0>119.0 (21)
204	Isofenphos	9.46	213.0>121.1 (15)	185.0>121.1 (15)
205	Isofenphos-methyl	9.28	199.0>121.1 (12)	199.0>93.1 (27)
206	Isoprocarb	6.58	136.0>121.1 (9)	121.0>103.1 (15)
207	Isopropalin	9.26	280.0>238.1 (9)	280.0>133.1 (18)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
208	Isoprothiolane	10.20	162.0>85.0 (18)	290.0>118.0 (12)
209	Isoxadifen-ethyl	11.29	294.0>204.1 (21)	222.0>178.1 (27)
210	Isoxathion	10.59	177.0>130.1 (9)	313.0>177.0 (9)
211	Kresoxim-methyl	10.42	116.0>89.1 (15)	206.0>116.1 (6)
212	Lactofen	13.23	344.0>222.9 (18)	344.0>179.1 (24)
213	Leptophos	12.91	171.0>77.1 (21)	171.0>124.1 (12)
214	Malathion	8.82	173.0>99.1 (18)	158.0>125.0 (9)
215	Mecarbam	9.51	329.0>131.1 (18)	296.0>196.1 (9)
216	Mefenacet	13.11	192.0>136.0 (15)	192.0>109.1 (27)
217	Mefenpyr-diethyl	12.01	253.0>189.0 (24)	299.0>253.0 (9)
218	Mepanipyrim	10.05	222.0>220.1 (24)	223.0>221.1 (27)
219	Mepronil	11.16	269.0>119.1 (15)	269.0>91.1 (30)
220	Metalaxyl	8.52	234.0>146.2 (21)	249.0>190.2 (6)
221	Metconazole	12.65	319.0>125.1 (24)	319.0>70.1 (21)
222	Methidathion	9.79	145.0>85.0 (9)	145.0>58.0 (15)
223	Methoprotryne	10.51	256.0>212.1 (15)	256.0>170.1 (24)
224	Methoxychlor	12.44	227.0>169.1 (27)	227.0>212.1 (18)
225	Metolachlor	8.91	238.0>162.2 (15)	238.0>133.1 (27)
226	Metrafenone	13.51	393.0>362.9 (18)	379.0>348.9 (21)
227	Metribuzin	8.37	198.0>82.1 (18)	198.0>110.1 (12)
228	Mevinphos	6.00	192.0>127.0 (12)	192.0>164.1 (6)
229	Mirex	13.28	272.0>236.70 (24)	272.0>234.8 (21)
230	Molinate	6.64	187.0>126.1 (6)	187.0>55.1 (27)
231	Myclobutanil	10.40	179.0>125.0 (18)	150.0>123.0 (18)
232	Napropamide	10.12	271.0>128.1 (6)	271.0>72.1 (21)
233	Nitrapyrin	6.15	194.0>133.0 (18)	194.0>158.0 (21)
234	Nitrothal-isopropyl	9.10	236.0>194.0 (12)	194.0>148.0 (12)
235	Nonachlor-*cis*	10.98	409.0>299.8 (24)	407.0>299.9 (30)
236	Nonachlor-*trans*	10.08	409.0>299.8 (24)	407.0>299.9 (30)
237	Norflurazon	11.40	303.0>145.1 (21)	145.0>95.1 (21)
238	Nuarimol	11.74	235.0>139.0 (15)	314.0>139.1 (15)
242	Ofurace	11.24	232.0>158.1 (18)	232.0>186.2 (12)
243	Omethoate	6.87	156.0>110.0 (9)	156.0>79.0 (21)
244	Oryzalin	10.38	317.0>299.70 (9)	317.0>222.9 (24)
245	Oxadiazon	10.31	258.0>175.0 (9)	302.0>175.0 (15)
246	Oxadixyl	10.93	163.0>132.1 (9)	163.0>117.1 (24)
247	Oxyfluorfen	10.38	252.0>146.1 (30)	252.0>170.1 (30)
251	Paclobutrazol	9.91	236.0>125.0 (12)	236.0>167.0 (9)
252	Parathion	9.02	291.0>109.0 (15)	291.0>81.0 (27)
253	Parathion-methyl	8.44	263.0>109.0 (15)	263.0>246.0 (6)
254	Pebulate	6.20	128.0>57.1 (9)	161.0>128.1 (6)
255	Penconazole	9.46	248.0>157.1 (27)	159.0>123.0 (18)
256	Pencycuron	7.36	180.0>125.1 (9)	125.0>89.1 (18)
257	Pendimethalin	9.36	252.0>162.1 (12)	252.0>191.1 (9)
258	Pentachloroaniline	8.25	265.0>194.1 (21)	263.0>191.9 (21)
259	Pentachlorothioanisole	8.84	296.0>262.70 (18)	263.0>192.9 (30)
260	Penthiopyrad	10.89	302.0>177.1 (21)	177.0>101.0 (15)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
261-1	Permethrin-1	13.95	183.0>153.1 (15)	183.0>165.1 (12)
261-2	Permethrin-2	14.08	183.0>153.1 (15)	183.0>165.1 (12)
262-1	Phenothrin-1	12.63	123.0>81.1 (9)	123.0>79.1 (18)
262-2	Phenothrin-2	12.82	123.0>81.1 (9)	123.0>79.1 (18)
263	Phenthoate	9.56	274.0>121.1 (12)	246.0>121.1 (6)
264	Phorate	7.35	260.0>75.1 (15)	231.0>129.0 (24)
265	Phosalone	12.89	182.0>75.1 (30)	182.0>102.1 (18)
266	Phosmet	12.29	160.0>77.1 (27)	160.0>133.1 (15)
267-1	Phosphamidon-1	7.84	127.0>109.0 (15)	264.0>127.1 (15)
267-2	Phosphamidon-2	8.25	127.0>109.1 (15)	264.0>127.0 (15)
268	Phthalide	9.21	243.0>214.8 (21)	272.0>242.9 (12)
269	Picolinafen	12.37	376.0>238.1 (24)	238.0>145.1 (24)
270	Picoxystrobin	9.95	335.0>173.1 (12)	303.0>157.1 (24)
271	Piperonyl butoxide	11.88	176.0>131.1 (15)	176.0>117.1 (21)
272	Piperophos	12.36	320.0>122.1 (15)	320.0>82.1 (30)
273	Pirimicarb	8.09	238.0>166.1 (12)	166.0>55.0 (24)
274	Pirimiphos ethyl	9.18	318.0>166.2 (15)	333.0>180.1 (9)
275	Pirimiphos methyl	8.68	290.0>125.1 (24)	276.0>125.1 (18)
276	Pretilachlor	10.22	262.0>202.1 (12)	238.0>146.1 (12)
277	Prochloraz	14.15	308.0>70.1 (15)	308.0>85.1 (12)
278	Procymidone	9.64	283.0>96.1 (12)	285.0>96.1 (12)
279	Profenofos	10.26	339.0>268.8 (18)	339.0>310.8 (9)
280	Profluralin	7.70	318.0>199.0 (18)	330.0>69.0 (18)
281	Promecarb	7.32	150.0>135.1 (12)	135.0>115.1 (15)
282	Prometon	7.57	210.0>168.1 (9)	225.0>183.1 (6)
283	Prometryn	8.56	226.0>184.1 (9)	241.0>58.1 (15)
284	Propachlor	6.94	176.0>57.1 (9)	176.0>120.0 (12)
285	Propanil	8.34	217.0>161.0 (9)	161.0>99.0 (24)
286	Propaquizafop	17.84	443.0>299.0 (21)	371.0>10.1 (12)
287	Propargite	11.80	135.0>107.1 (15)	135.0>77.1 (27)
288	Propazine	7.66	214.0>172.0 (12)	229.0>58.0 (15)
289	Propetamphos	7.73	236.0>194.0 (6)	236.0>166.0 (15)
290	Propham	6.19	179.0>137.1 (6)	179.0>93.1 (15)
291-1	Propiconazole-1	11.43	259.0>69.1 (15)	259.0>173.0 (18)
291-2	Propiconazole-2	11.43	259.0>69.1 (15)	259.0>173.0 (18)
292	Propisochlor	8.49	162.0>120.1 (15)	162.0>144.1 (12)
293	Propyzamide	7.81	173.0>109.0 (27)	254.0>191.1 (18)
294	Prosulfocarb	8.66	251.0>128.1 (6)	251.0>86.1 (15)
295	Prothiofos	10.20	267.0>238.9 (12)	309.0>239.0 (18)
296	Pyracarbolid	9.25	217.0>125.1 (9)	125.0>107.1 (6)
297	Pyraclofos	13.64	194.0>138.1 (21)	360.0>194.1 (15)
298	Pyraclostrobin	15.72	164.0>132.1 (15)	132.0>77.1 (21)
299	Pyrazophos	13.37	221.0>193.1 (12)	265.0>138.1 (30)
300	Pyributicarb	12.06	165.0>108.1 (18)	165.0>93.1 (27)
301	Pyridaben	14.09	147.0>117.1 (21)	147.0>132.1 (15)
302	Pyridalyl	15.12	204.0>148.1 (21)	204.0>146.1 (27)
303	Pyridaphenthion	12.16	340.0>199.1 (9)	199.0>92.1 (15)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
304	Pyrifenox	9.86	187.0>124.1 (24)	262.0>64.0 (30)
305	Pyrimethanil	7.90	198.0>156.1 (24)	198.0>118.1 (30)
306	Pyrimidifen	15.46	184.0>169.1 (21)	184.0>86.0 (27)
307	Pyriminobac-methyl (*E*)	11.45	302.0>256.1 (18)	302.0>230.1 (18)
308	Pyriminobac-methyl (*Z*)	10.78	302.0>256.1 (18)	302.0>230.0 (18)
309	Pyriproxyfen	13.05	226.0>186.1 (15)	226.0>77.1 (30)
310	Pyroquilon	7.87	173.0>130.1 (21)	130.0>77.1 (24)
311	Quinalphos	9.58	146.0>118.1 (12)	157.0>102.1 (24)
312	Quinoxyfen	11.46	237.0>208.0 (30)	272.0>237.0 (21)
313	Quintozene	7.72	295.0>236.8 (18)	237.0>142.9 (24)
314	Quizalofop-ethyl	14.94	372.0>299.1 (15)	299.0>192.1 (30)
315	Resmethrin	11.92	171.0>128.1 (15)	171.0>143.1 (6)
316	Secbumeton	8.00	169.0>154.2 (9)	196.0>85.1 (15)
317	Silafluofen	15.22	286.0>258.1 (12)	286.0>207.1 (15)
318	Simazine	7.59	201.0>173.1 (6)	173.0>138.2 (9)
319	Simeconazole	8.44	211.0>195.1 (6)	211.0>121.1 (15)
320	Simetryn	8.50	213.0>185.1 (9)	213.0>170.1 (9)
321	Spirodiclofen	13.83	312.0>109.1 (21)	312.0>259.1 (12)
322	Spiromesifen	12.04	272.0>254.1 (9)	272.0>185.1 (24)
323	Sulfotep	7.22	238.0>146.0 (15)	322.0>146.0 (27)
324	Sulprofos	11.19	322.0>156.0 (9)	322.0>139.0 (15)
325	Tebuconazole	11.77	250.0>125.1 (21)	125.0>89.1 (15)
326	Tebufenpyrad	12.57	333.0>171.1 (21)	335.0>173.1 (18)
327	Tebupirimfos	8.07	318.0>152.2 (15)	276.0>234.0 (6)
328	Tecnazene	6.88	261.0>202.9 (15)	215.0>178.9 (12)
329	Tefluthrin	7.94	177.0>127.0 (18)	197.0>141.1 (15)
330	Tepraloxydim	11.41	164.0>108.1 (9)	164.0>81.1 (21)
331	Terbacil	7.98	161.0>88.0 (24)	117.0>76.0 (6)
332	Terbufos	7.77	231.0>129.0 (24)	231.0>174.9 (15)
333	Terbumeton	7.68	225.0>169.2 (6)	169.0>112.1 (15)
334	Terbuthylazine	7.77	229.0>173.1 (9)	214.0>71.1 (18)
335	Terbutryn	8.73	241.0>185.1 (6)	226.0>96.1 (18)
336	Tetrachlorvinphos	9.87	329.0>109.1 (21)	331.0>109.1 (18)
337	Tetraconazole	9.05	336.0>204.1 (27)	336.0>164.1 (24)
338	Tetradifon	12.80	356.0>159.0 (15)	356.0>228.9 (9)
339	Thenylchlor	11.69	127.0>53.0 (21)	288.0>141.1 (15)
340	Thiazopyr	8.84	327.0>277.0 (30)	363.0>30.0 (15)
341	Thifluzamide	10.34	447.0>426.8 (18)	447.0>399.8 (27)
342	Thiobencarb	8.95	10.0>72.1 (6)	125.0>89.1 (15)
343	Thiometon	7.47	158.0>125.0 (6)	246.0>88.1 (6)
344	Tolclofos-methyl	8.45	265.0>249.9 (12)	265.0>93.1 (24)
345	Tolfenpyrad	17.49	197.0>154.1 (12)	197.0>169.1 (9)
346	Tolylfluanid	9.49	238.0>137.1 (15)	181.0>138.1 (12)
347	Triadimefon	9.07	208.0>111.1 (21)	208.0>127.0 (15)
348	Triadimenol	9.64	168.0>70.1 (15)	128.0>65.1 (21)
349	Tri-allate	8.04	268.0>184.0 (21)	270.0>186.0 (21)
350	Triazophos	11.18	257.0>162.1 (9)	285.0>162.1 (15)

No.	Pesticide name	t_R (min)	precursor ion > product ion (CE, V)	
			quantifier	qualifier
351	Tribufos	10.35	202.0>147.0 (6)	202.0>112.9 (18)
352	Tricyclazole	10.51	189.0>162.0 (15)	189.0>135.0 (24)
353	Trifloxystrobin	11.37	116.0>89.1 (15)	116.0>63.1 (27)
354	Triflumizole	9.65	278.0>73.1 (6)	287.0>68.1 (9)
355	Trifluralin	7.17	306.0>264.0 (9)	264.0>160.1 (15)
356	Triticonazole	12.90	217.0>167.2 (21)	235.0>182.2 (15)
357	Uniconazole	10.42	234.0>165.0 (12)	234.0>137.0 (18)
358	Vernolate	6.12	128.0>86.1 (6)	203.0>128.1 (6)
359	Vinclozolin	8.40	212.0>172.0 (15)	285.0>212.1 (15)
360	Zoxamide	12.01	258.0>187.0 (12)	187.0>123.0 (24)
-	*BHC, α-d_6(ISTD)	7.39	187.0>150.0 (18)	224.0>150.1 (18)
-	*Chlorpyrifos-d_{10} (ISTD)	8.88	324.0>259.8 (21)	292.0>260.1 (15)
-	*TDCPP (ISTD)	11.27	191.0>75.0 (9)	381.0>159.1 (15)
-	*TPP (ISTD)	11.83	326.0>169.0 (28)	326.0>215.0 (28)

Table S2. Matrix-dependent limits of quantitation (LOQs), linearity, and matrix effects (MEs) of 360 pesticides in matrices (brown rice, orange, spinach, and potato)

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
1	2,6-Diisopropylnaphthalene	10.0	0.9959	10.0	0.9973	10.0	0.9999	10.0	0.9975
2	Acetochlor	5.0	0.9990	10.0	0.9994	2.5	0.9994	10.0	0.9997
3	Acibenzolar-S-methyl	10.0	0.9990	25.0	0.9973	10.0	0.9989	10.0	0.9957
4	Acrinathrin	2.5	0.9997	1.0	0.9971	1.0	0.9956	1.0	0.9942
5	Alachlor	1.0	0.9999	2.5	0.9997	1.0	0.9996	1.0	0.9999
6	Aldrin	1.0	0.9980	10.0	0.9975	1.0	0.9969	5.0	0.9988
7	Allidochlor	1.0	0.9968	1.0	0.9945	1.0	0.9998	1.0	0.9988
8	Ametoctradin	10.0	0.9940	1.0	0.9976	5.0	0.9989	25.0	0.9999
9	Ametryn	2.5	0.9996	1.0	0.9998	2.5	0.7392	2.5	0.9990
10	Anilofos	1.0	0.9995	1.0	0.9994	1.0	0.9993	1.0	0.9995
11	Atrazine	1.0	0.9998	1.0	0.9996	1.0	0.9993	1.0	0.9996
12	Azaconazole	1.0	0.9995	2.5	0.9999	1.0	0.9997	1.0	0.9999
13	Azinphos-ethyl	5.0	0.9997	2.5	0.9986	2.5	0.9993	1.0	0.9989
14	Azinphos-methyl	10.0	0.9989	10.0	0.9950	10.0	0.9971	5.0	0.9913
15	Azoxystrobin	1.0	0.9996	1.0	0.9998	1.0	0.9994	1.0	0.9995
16	Benalaxyl	2.5	0.9994	1.0	1.0000	1.0	0.9988	1.0	1.0000
17	Bendiocarb	5.0	0.9968	5.0	0.9956	5.0	0.9993	2.5	0.9876
18	Benfuresate	5.0	0.9993	1.0	0.9969	2.5	0.9986	2.5	0.9993
19	Benodanil	1.0	0.9991	5.0	0.9937	1.0	0.9985	2.5	0.9992
20	Benthiavalicarb-isopropyl	5.0	0.9991	5.0	0.9997	10.0	0.9993	1.0	0.9996
21	Benzoylprop-ethyl	1.0	0.9986	1.0	0.9998	1.0	0.9996	1.0	0.9999
22	BHC, alpha-	1.0	0.9989	1.0	0.9983	1.0	0.9999	1.0	0.9998
23	BHC, beta-	1.0	0.9995	1.0	0.9986	1.0	0.9996	1.0	0.9999
24	BHC, delta-	1.0	0.9991	1.0	0.9994	1.0	0.9993	1.0	0.9936
25	BHC, gamma-	1.0	0.9991	1.0	0.9989	1.0	0.9992	1.0	0.9995

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
26	Bifenazate	1.0	0.9996	2.5	0.9994	1.0	0.9993	1.0	0.9994
27	Bifenox	1.0	0.9994	1.0	0.9969	1.0	0.9923	1.0	0.9991
28	Bifenthrin	1.0	0.9995	1.0	0.9999	1.0	0.9993	1.0	0.9998
29	Binapacryl	-	N.D.	-	0.8640	-	0.1459	-	0.5669
30	Bitertanol	1.0	0.9997	1.0	0.9998	1.0	0.9994	1.0	0.9998
31	Bixafen	1.0	0.9986	1.0	0.9993	1.0	0.9996	1.0	0.9999
32	Boscalid	1.0	0.9998	1.0	0.9998	1.0	0.9993	1.0	0.9994
33	Bromacil	5.0	0.9988	5.0	0.9992	2.5	0.9981	25.0	0.9812
34	Bromobutide	10.0	0.9995	25.0	0.9964	1.0	0.9989	1.0	0.9995
35	Bromophos	1.0	0.9986	1.0	0.9990	1.0	0.9995	1.0	0.9995
36	Bromopropylate	1.0	0.9995	1.0	1.0000	1.0	0.9986	1.0	1.0000
37	Bupirimate	1.0	0.9975	2.5	0.9999	2.5	0.9424	1.0	0.9997
38	Buprofezin	10.0	0.9986	2.5	0.9993	5.0	0.9993	2.5	0.9995
39	Butachlor	5.0	0.9992	2.5	0.9998	2.5	0.9991	2.5	0.9998
40	Butafenacil	1.0	0.9991	1.0	0.9998	1.0	0.9992	1.0	0.9994
41	Butralin	1.0	0.9993	1.0	0.9982	1.0	0.9971	1.0	0.9990
42	Butylate	10.0	0.9935	10.0	0.9908	25.0	0.9994	10.0	0.9987
43	Cadusafos	1.0	0.9992	1.0	0.9991	1.0	0.9999	2.5	0.9999
44	Cafenstrole	2.5	0.9978	10.0	0.9912	2.5	0.9984	1.0	0.9747
45	Captafol	-	0.2970	-	0.3524	-	0.0011	-	0.3760
46	Captan	-	0.4031	-	0.4247	-	0.0075	-	0.8622
47	Carbaryl	2.5	0.9975	5.0	0.9949	10.0	0.9989	5.0	0.8653
48	Carbofuran	5.0	0.9991	25.0	0.9991	25.0	0.9991	10.0	0.9945
49	Carbophenothion	1.0	0.9992	1.0	0.9996	1.0	0.9993	1.0	1.0000
50	Carbosulfan	25.0	0.9905	2.5	0.9994	25.0	0.9846	1.0	0.9998
51	Carboxin	1.0	0.9982	1.0	0.9999	1.0	0.9991	1.0	0.9992
52	Chinomethionat	2.5	0.9993	2.5	0.9975	1.0	0.9995	1.0	0.9840
53	Chlordane-cis	1.0	0.9990	1.0	0.9996	1.0	0.9988	1.0	0.9995
54	Chlordane-trans	1.0	0.9978	1.0	0.9983	1.0	0.9996	1.0	0.9997

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
55	Chlorethoxyfos	10.0	0.9975	10.0	0.9953	25.0	0.9998	10.0	0.9991
56	Chlorfenapyr	2.5	0.9970	2.5	0.9971	1.0	0.9962	2.5	0.9937
57	Chlorfenson	2.5	0.9929	1.0	0.9997	1.0	0.9991	1.0	0.9991
58	Chlorfenvinphos	1.0	0.9994	1.0	0.9997	1.0	0.9994	1.0	0.9999
59	Chlorfluazuron	2.5	0.9961	1.0	0.9989	1.0	0.9993	2.5	0.9994
60	Chlorflurenol-methyl	1.0	0.9993	1.0	0.9996	1.0	0.9993	1.0	0.9998
61	Chlorobenzilate and chloropropylate	1.0	0.9996	1.0	0.9998	1.0	0.9990	1.0	0.9999
62	Chloroneb	1.0	0.9979	1.0	0.9978	1.0	0.9998	1.0	0.9985
63	Chlorothalonil	1.0	0.9981	2.5	0.9914	1.0	0.9739	1.0	0.8617
64	Chlorpropham	1.0	0.9979	1.0	0.9978	1.0	0.9992	1.0	0.9991
65	Chlorpyrifos	1.0	0.9991	1.0	0.9999	1.0	0.9997	1.0	0.9998
66	Chlorpyrifos-methyl	1.0	0.9989	1.0	0.9998	1.0	0.9993	1.0	1.0000
67	Chlorthal-dimethyl	1.0	0.9983	1.0	0.9997	1.0	0.9993	1.0	0.9995
68	Chlorthiophos	1.0	0.9993	1.0	0.9999	1.0	0.9997	1.0	0.9997
69	Chlozolinate	2.5	0.9984	5.0	0.9990	2.5	0.9990	2.5	0.9994
70	Cinmethylin	50.0	0.9996	50.0	0.9912	10.0	0.9987	25.0	0.9991
71	Clomazone	1.0	0.9994	2.5	0.9994	1.0	0.9994	1.0	0.9997
72	Clomeprop	1.0	0.9997	5.0	0.9996	1.0	0.9989	1.0	0.9999
73	Coumaphos	1.0	0.9996	1.0	0.9995	1.0	0.9995	1.0	0.9991
74	Cyanazine	5.0	0.9998	2.5	0.9959	2.5	0.9970	1.0	0.9972
75	Cyanophos	1.0	0.9990	1.0	0.9996	1.0	0.9989	1.0	0.9993
76	Cycloate	10.0	0.9967	10.0	0.9959	5.0	0.9998	5.0	0.9992
77	Cyflufenamid	1.0	0.9962	1.0	0.9979	1.0	0.9972	1.0	0.9988
78	Cyflumetofen	1.0	0.9978	2.5	0.9990	1.0	0.9978	1.0	0.9617
79	Cyfluthrin	5.0	0.9997	5.0	0.9993	1.0	0.9985	5.0	0.9965
80	Cyhalofop-butyl	1.0	0.9995	1.0	0.9998	1.0	0.9989	1.0	0.9998
81	Cyhalothrin	5.0	0.9991	5.0	0.9976	10.0	0.9964	5.0	0.9991
82	Cypermethrin	5.0	0.9997	5.0	0.9989	1.0	0.9987	5.0	0.9991
83	Cyproconazole	2.5	0.9994	2.5	0.9996	2.5	0.9996	1.0	0.9989

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
84	Cyprodinil	1.0	0.9992	1.0	0.9998	2.5	0.9993	2.5	0.9996
85	DDD, o, p'-	1.0	0.9983	1.0	0.9994	1.0	0.9997	1.0	0.9999
86	DDD, p, p'-	1.0	0.9992	1.0	0.9997	1.0	0.9994	1.0	0.9999
87	DDE, o, p'-	1.0	0.9991	1.0	0.9998	1.0	0.9994	1.0	0.9999
88	DDE, p, p'-	1.0	0.9988	1.0	0.9999	1.0	0.9992	1.0	0.9997
89	DDT, o, p'-	1.0	0.9945	1.0	0.9980	1.0	0.9988	1.0	0.9994
90	DDT, p, p'-	1.0	0.9903	1.0	0.9934	1.0	0.9981	1.0	0.9982
91	Deltamethrin	5.0	0.9976	2.5	0.9926	2.5	0.9955	1.0	0.9891
92	Desmetryn	1.0	0.9993	1.0	0.9996	2.5	0.9996	1.0	0.9998
93	Di-Allate	1.0	0.9986	1.0	0.9971	1.0	0.9993	1.0	0.9995
94	Diazinon	1.0	0.9993	5.0	0.9993	1.0	0.9987	1.0	0.9972
95	Dichlobenil	1.0	0.9965	1.0	0.9947	1.0	0.9998	1.0	0.9994
96	Dichlofenthion	1.0	0.9994	1.0	0.9997	1.0	0.9995	1.0	0.9999
97	Dichlofluanid	5.0	0.9928	5.0	0.9896	5.0	0.9857	2.5	0.9951
98	Dichlormid	1.0	0.9977	1.0	0.9951	1.0	0.9998	1.0	0.9992
99	Dichlorvos	1.0	0.9964	1.0	0.9940	1.0	0.9975	1.0	0.9977
100	Diclofop-methyl	1.0	0.9992	1.0	0.9999	1.0	0.9997	1.0	0.9996
101	Dicloran	2.5	0.9974	10.0	0.9987	5.0	0.9993	10.0	0.9997
102	Dicofol	1.0	0.9992	2.5	0.9996	1.0	0.9994	1.0	0.9991
103	Dicrotophos	5.0	0.9990	5.0	0.9958	2.5	0.9983	1.0	0.9980
104	Dieldrin	10.0	0.9973	5.0	0.9991	5.0	0.9982	2.5	0.9986
105	Diethatyl-ethyl	2.5	0.9994	1.0	0.9997	1.0	0.9987	1.0	0.9997
106	Diethofencarb	2.5	0.9993	2.5	0.9996	2.5	0.9994	2.5	0.9997
107	Difenoconazole	1.0	0.9996	1.0	0.9999	1.0	0.9992	1.0	0.9999
108	Diflufenican	1.0	0.9995	1.0	0.9998	1.0	0.9991	1.0	0.9999
109	Dimepiperate	1.0	0.9990	1.0	0.9997	1.0	0.9992	1.0	0.9998
110	Dimethachlor	1.0	0.9983	5.0	0.9929	2.5	0.9998	1.0	0.9997
111	Dimethametryn	2.5	0.9996	1.0	0.9999	2.5	0.9633	1.0	0.9998
112	Dimethenamid	1.0	0.9995	1.0	0.9997	1.0	0.9995	1.0	0.9999

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
113	Dimethipin	2.5	0.9974	10.0	0.9974	5.0	0.9986	10.0	0.9915
114	Dimethoate	10.0	0.9958	5.0	0.9989	1.0	0.9976	2.5	0.9944
115	Dimethomorph	1.0	0.9994	1.0	0.9999	1.0	0.9994	1.0	0.9998
116	Dimethylvinphos	1.0	0.9989	1.0	0.9998	1.0	0.9968	1.0	0.9977
117	Diniconazole	1.0	0.9997	2.5	0.9998	1.0	0.9990	1.0	0.9996
118	Dinitramine	1.0	0.9985	1.0	0.9994	1.0	0.9970	1.0	0.9960
119	Dioxathion	1.0	0.9981	1.0	0.9992	1.0	0.9984	1.0	0.9985
120	Diphenamid	2.5	0.9997	5.0	0.9999	2.5	0.9998	2.5	0.9999
121	Diphenylamine	1.0	0.9927	1.0	0.9971	1.0	0.9998	1.0	0.9936
122	Disulfoton	5.0	0.9989	5.0	0.9996	5.0	0.9995	5.0	0.9994
123	Dithiopyr	1.0	0.9992	1.0	0.9999	1.0	0.9995	1.0	0.9996
124	Edifenphos	1.0	0.9984	1.0	0.9988	1.0	0.9984	1.0	0.9955
125	Endosulfan, alpha-	2.5	0.9993	1.0	0.9993	1.0	0.9979	1.0	0.9969
126	Endosulfan, beta-	1.0	0.9993	1.0	0.9971	1.0	0.9988	1.0	0.9986
127	Endosulfan, sulfate-	1.0	0.9993	1.0	0.9997	1.0	0.9992	1.0	0.9998
128	Endrin	5.0	0.9780	2.5	0.9937	5.0	0.9875	5.0	0.9977
129	EPN	1.0	0.9997	1.0	0.9974	1.0	0.9961	2.5	0.9998
130	Epoxiconazole	1.0	0.9994	1.0	0.9998	1.0	0.9994	1.0	1.0000
131	EPTC	5.0	0.9930	1.0	0.9915	2.5	0.9996	10.0	0.9990
132	Esprocarb	1.0	0.9995	1.0	0.9996	1.0	0.9995	1.0	0.9999
133	Etaconazole	1.0	0.9992	1.0	0.9990	1.0	0.9994	1.0	0.9998
134	Ethalfluralin	1.0	0.9983	1.0	0.9975	1.0	0.9983	1.0	1.0000
135	Ethiofencarb	2.5	0.9982	1.0	0.9955	2.5	0.9972	2.5	0.9535
136	Ethion	1.0	0.9994	1.0	0.9998	1.0	0.9993	1.0	0.9996
137	Ethofumesate	1.0	0.9997	5.0	0.9997	1.0	0.9995	1.0	0.9997
138	Ethoprophos	1.0	0.9973	1.0	0.9993	1.0	0.9997	1.0	0.9991
139	Ethoxyquin	1.0	0.9995	1.0	0.9992	1.0	0.9996	1.0	0.9996
140	Etofenprox	1.0	0.9994	1.0	0.9997	1.0	0.9996	1.0	0.9998
141	Etoxazole	1.0	0.9995	1.0	0.9998	1.0	0.9991	1.0	0.9998

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
142	Etridiazole	1.0	0.9883	1.0	0.9941	1.0	0.9983	1.0	0.9992
143	Etrimfos	1.0	0.9991	1.0	0.9998	1.0	0.9992	1.0	0.9993
144	Fenamidone	1.0	0.9994	1.0	0.9993	1.0	0.9987	1.0	0.9994
145	Fenamiphos	1.0	0.9997	2.5	0.9996	1.0	0.9995	1.0	0.9987
146	Fenarimol	5.0	0.9997	1.0	0.9998	1.0	0.9996	1.0	0.9994
147	Fenazaquin	1.0	0.9995	1.0	0.9999	1.0	0.9993	1.0	0.9998
148	Fenbuconazole	1.0	0.9988	1.0	0.9995	1.0	0.9987	1.0	0.9995
149	Fenchlorphos	1.0	0.9993	1.0	0.9999	1.0	0.9999	1.0	0.9999
150	Fenclorim	1.0	0.9991	1.0	0.9985	1.0	0.9997	1.0	0.9991
151	Fenfuram	1.0	0.9994	1.0	0.9997	1.0	0.9997	1.0	0.9988
152	Fenhexamid	1.0	0.9996	1.0	0.9995	1.0	0.9982	1.0	0.9939
153	Fenitrothion	1.0	0.9997	1.0	0.9978	1.0	0.9977	1.0	0.9997
154	Fenobucarb	5.0	0.9988	50.0	0.9909	10.0	0.9995	5.0	0.9794
155	Fenothiocarb	1.0	0.9982	1.0	0.9998	1.0	0.9994	1.0	0.9953
156	Fenoxanil	1.0	0.9994	1.0	0.9991	1.0	0.9988	1.0	0.9980
157	Fenpiclonil	5.0	0.9974	5.0	0.9981	1.0	0.9994	50.0	0.9969
158	Fenpropathrin	1.0	0.9992	2.5	0.9997	1.0	0.9989	1.0	0.9996
159	Fenpyrazamine	5.0	0.9994	5.0	0.9979	5.0	0.9975	2.5	0.9980
160	Fenson	1.0	0.9991	1.0	0.9997	1.0	0.9991	1.0	0.9996
161	Fensulfothion	1.0	0.9999	2.5	0.9996	1.0	0.9993	1.0	0.9984
162	Fenthion	2.5	0.9994	1.0	0.9996	1.0	0.9987	1.0	0.9999
163	Fenvalerate	5.0	0.9997	10.0	0.9989	5.0	0.9979	2.5	0.9990
164	Fipronil	1.0	0.9988	1.0	0.9999	1.0	0.9988	1.0	0.9997
165	Flonicamid	2.5	0.9995	5.0	0.9996	1.0	0.9987	2.5	0.9936
166	Fluacrypyrim	2.5	0.9993	2.5	0.9996	2.5	0.9997	1.0	0.9998
167	Fluazifop-butyl	1.0	0.9992	1.0	0.9998	1.0	0.9992	1.0	0.9997
168	Fluazinam	2.5	0.9895	2.5	0.9848	10.0	0.9934	25.0	0.8706
169	Fluchloralin	1.0	0.9995	1.0	0.9972	1.0	0.9960	1.0	0.9997
170	Flucythrinate	1.0	0.9995	1.0	0.9979	1.0	0.9979	1.0	0.9999

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
171	Fludioxonil	2.5	0.9994	2.5	0.9998	1.0	0.9991	10.0	0.9995
172	Flufenacet	5.0	0.9996	2.5	0.9993	5.0	0.9995	2.5	0.9972
173	Flumetralin	1.0	0.9996	1.0	0.9982	1.0	0.9976	1.0	0.9988
174	Flumiclorac-pentyl	1.0	0.9998	1.0	0.9995	1.0	0.9994	1.0	0.9999
175	Flumioxazin	1.0	0.9991	1.0	0.9972	1.0	0.9960	5.0	0.9947
176	Fluopicolide	1.0	0.9997	1.0	0.9998	2.5	0.9990	1.0	0.9992
177	Fluopyram	5.0	0.9995	2.5	0.9997	1.0	0.9995	1.0	1.0000
178	Fluquinconazole	1.0	0.9996	1.0	0.9997	1.0	0.9996	1.0	0.9996
179	Flurochloridone	2.5	0.9988	1.0	0.9970	5.0	0.9996	2.5	0.9987
180	Flurtamone	1.0	0.9955	1.0	0.9998	1.0	0.9991	2.5	0.9998
181	Flusilazole	1.0	0.9988	2.5	0.9995	1.0	0.9948	1.0	0.9991
182	Fluthiacet-methyl	1.0	0.9987	1.0	0.9925	1.0	0.9987	2.5	0.9729
183	Flutianil	1.0	0.9992	1.0	0.9998	1.0	0.9994	1.0	0.9993
184	Flutolanil	1.0	0.9989	1.0	0.9998	1.0	0.9998	1.0	0.9998
185	Flutriafol	2.5	0.9956	1.0	0.9999	2.5	0.9996	1.0	1.0000
186	Fluvalinate	2.5	0.9994	2.5	0.9975	1.0	0.9966	1.0	0.9839
187	Folpet	5.0	0.9932	5.0	0.9848	5.0	0.9972	1.0	0.9615
188	Fonofos	1.0	0.9994	1.0	0.9994	1.0	0.9996	1.0	0.9996
189	Formothion	1.0	0.9997	2.5	0.9945	1.0	0.9995	1.0	0.9774
190	Fosthiazate	1.0	0.9989	5.0	0.9993	1.0	0.9978	1.0	0.9934
191	Furathiocarb	2.5	0.9978	2.5	0.9992	10.0	0.9994	1.0	0.9975
192	Halfenprox	1.0	0.9997	1.0	0.9965	1.0	0.9944	1.0	0.9963
193	Heptachlor	1.0	0.9981	1.0	0.9989	1.0	0.9998	1.0	0.9993
194	Heptachlor epoxide	1.0	0.9994	1.0	0.9993	1.0	0.9995	1.0	0.9997
195	Heptenophos	1.0	0.9989	1.0	0.9985	1.0	0.9998	1.0	0.9986
196	Hexachlorobenzene	1.0	0.9977	1.0	0.9982	1.0	0.9992	1.0	0.9985
197	Hexaconazole	10.0	0.9984	5.0	0.9980	5.0	0.9989	2.5	0.9993
198	Hexazinone	1.0	0.9995	1.0	0.9998	2.5	0.9997	1.0	0.9997
199	Hexythiazox	25.0	0.9904	2.5	0.9993	2.5	0.9992	1.0	0.9994

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
200	Imazalil	10.0	0.9974	-	0.0270	-	0.0018	-	0.0682
201	Imibenconazole	1.0	0.9997	1.0	0.9995	1.0	0.9997	1.0	0.9997
202	Indanofan	1.0	0.9993	1.0	0.9991	1.0	0.9994	1.0	0.9991
203	Indoxacarb	10.0	0.9995	10.0	0.9968	10.0	0.9995	2.5	0.9946
204	Ipconazole	2.5	0.9995	5.0	0.9988	5.0	0.9992	2.5	0.9991
205	Ipfencarbazone	2.5	0.9996	2.5	0.9998	1.0	0.9993	1.0	0.9955
206	Iprobenfos	1.0	0.9995	1.0	0.9997	1.0	0.9993	1.0	0.9999
207	Iprodione	5.0	0.9995	1.0	0.9960	1.0	0.9981	1.0	0.9516
208	Iprovalicarb	10.0	0.9987	5.0	0.9998	10.0	0.9987	10.0	0.9995
209	Isazofos	1.0	0.9991	1.0	0.9996	1.0	0.9987	1.0	0.9991
210	Isofenphos	1.0	0.9987	1.0	0.9999	1.0	0.9989	1.0	0.9998
211	Isofenphos-methyl	1.0	0.9994	1.0	0.9999	1.0	0.9990	1.0	0.9999
212	Isoprocarb	2.5	0.9969	50.0	0.9982	1.0	0.9994	1.0	0.9987
213	Isopropalin	1.0	0.9991	1.0	0.9984	1.0	0.9973	1.0	0.9991
214	Isoprothiolane	2.5	0.9965	1.0	0.9999	2.5	0.9995	1.0	0.9996
215	Isoxadifen-ethyl	1.0	0.9999	1.0	0.9996	1.0	0.9984	1.0	0.9999
216	Isoxathion	5.0	0.9991	5.0	0.9952	5.0	0.9950	2.5	0.9996
217	Kresoxim-methyl	1.0	0.9989	2.5	0.9998	1.0	0.9997	1.0	0.9999
218	Lactofen	1.0	0.9981	1.0	0.9931	1.0	0.9863	1.0	0.9997
219	Leptophos	1.0	0.9994	1.0	0.9995	1.0	0.9993	1.0	0.9999
220	Malathion	1.0	0.9996	1.0	0.9997	1.0	0.9989	1.0	0.9995
221	Mecarbam	2.5	0.9984	1.0	0.9994	1.0	0.9993	1.0	0.9980
222	Mefenacet	1.0	0.9994	1.0	0.9997	1.0	0.9991	1.0	0.9994
223	Mefenpyr-diethyl	1.0	0.9990	1.0	0.9999	1.0	0.9994	1.0	0.9998
224	Mepanipyrim	25.0	0.9996	1.0	0.9999	2.5	0.9989	1.0	0.9997
225	Mepronil	1.0	0.9995	1.0	0.9999	1.0	0.9994	1.0	0.9986
226	Metalaxyl	1.0	0.9993	1.0	0.9991	1.0	0.9991	1.0	0.9993
227	Metconazole	5.0	0.9985	1.0	0.9911	5.0	0.9983	2.5	0.9925
228	Methidathion	1.0	0.9993	1.0	0.9998	1.0	0.9993	1.0	0.9990

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
229	Methoprotryne	1.0	0.9995	2.5	0.9997	1.0	0.9993	2.5	0.9995
230	Methoxychlor	2.5	0.9934	1.0	0.9957	2.5	0.9988	1.0	0.9995
231	Metolachlor	1.0	0.9996	1.0	0.9997	1.0	0.9997	1.0	0.9999
232	Metrafenone	1.0	0.9998	1.0	0.9998	1.0	0.9988	1.0	0.9994
233	Metribuzin	1.0	0.9993	1.0	0.9983	1.0	0.9989	2.5	0.9993
234	Mevinphos	1.0	0.9984	1.0	0.9974	1.0	0.9998	1.0	0.9994
235	Mirex	1.0	0.9998	1.0	0.9997	1.0	0.9990	1.0	0.9997
236	Molinate	1.0	0.9971	1.0	0.9944	1.0	0.9998	1.0	0.9995
237	Myclobutanil	1.0	0.9995	2.5	0.9994	1.0	0.9996	1.0	0.9998
238	Napropamide	1.0	0.9980	1.0	0.9995	1.0	0.9981	1.0	0.9999
239	Nitrapyrin	1.0	0.9813	1.0	0.9827	1.0	0.9988	5.0	0.9988
240	Nitrothal-isopropyl	1.0	0.9994	1.0	0.9977	1.0	0.9965	1.0	0.9992
241	Nonachlor-cis	1.0	0.9983	1.0	0.9993	1.0	0.9981	1.0	0.9994
242	Nonachlor-trans	1.0	0.9984	1.0	0.9997	1.0	0.9992	1.0	0.9977
243	Norflurazon	1.0	0.9987	1.0	0.9997	1.0	0.9990	5.0	0.9990
244	Nuarimol	2.5	0.9992	1.0	0.9998	1.0	0.9992	1.0	0.9998
245	Ofurace	1.0	0.9995	2.5	0.9993	1.0	0.9994	1.0	0.9972
246	Omethoate	2.5	0.9995	5.0	0.9954	1.0	0.9958	10.0	0.9585
247	Oryzalin	1.0	0.9996	1.0	0.9988	2.5	0.9968	1.0	0.9970
248	Oxadiazon	1.0	0.9985	1.0	0.9997	1.0	0.9997	1.0	0.9998
249	Oxadixyl	2.5	0.9996	1.0	0.9998	2.5	0.9996	1.0	0.9998
250	Oxyfluorfen	1.0	0.9984	2.5	0.9966	2.5	0.9964	2.5	0.9968
251	Paclobutrazol	2.5	0.9997	1.0	0.9999	2.5	0.9996	1.0	0.9997
252	Parathion	2.5	0.9996	1.0	0.9975	1.0	0.9967	1.0	0.9996
253	Parathion-methyl	1.0	0.9998	1.0	0.9967	1.0	0.9983	1.0	0.9996
254	Pebulate	5.0	0.9942	5.0	0.9930	1.0	0.9986	10.0	0.9986
255	Penconazole	1.0	0.9991	1.0	0.9996	1.0	0.9988	1.0	0.9997
256	Pencycuron	2.5	0.9921	5.0	0.9990	2.5	0.9112	1.0	0.9956
257	Pendimethalin	1.0	0.9986	1.0	0.9974	1.0	0.9956	1.0	0.9980

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
258	Pentachloroaniline	1.0	0.9989	1.0	0.9993	1.0	0.9995	1.0	0.9994
259	Pentachlorothioanisole	1.0	0.9992	1.0	0.9987	1.0	1.0000	1.0	0.9981
260	Penthiopyrad	1.0	0.9996	1.0	0.9997	1.0	0.9997	1.0	0.9996
261	Permethrin	1.0	0.9994	25.0	0.9993	1.0	0.9927	10.0	0.9994
262	Phenothrin	1.0	0.9142	1.0	0.9431	1.0	0.9975	50.0	0.9988
263	Phenthoate	1.0	0.9994	1.0	0.9996	1.0	0.9994	1.0	0.9999
264	Phorate	1.0	0.9969	1.0	0.9980	1.0	0.9993	1.0	0.9996
265	Phosalone	2.5	0.9993	2.5	0.9993	1.0	0.9990	1.0	0.9998
266	Phosmet	1.0	0.9993	5.0	0.9959	1.0	0.9994	1.0	0.9908
267	Phosphamidon	5.0	0.9989	5.0	0.9964	10.0	0.9977	5.0	0.9966
268	Phthalide	1.0	0.9996	1.0	0.9999	1.0	0.9996	1.0	0.9997
269	Picolinafen	1.0	0.9993	1.0	0.9996	1.0	0.9994	1.0	0.9999
270	Picoxystrobin	1.0	0.9992	1.0	0.9998	1.0	0.9994	1.0	0.9998
271	Piperonyl butoxide	1.0	0.9994	1.0	0.9998	1.0	0.9994	1.0	0.9998
272	Piperophos	1.0	0.9992	1.0	0.9998	1.0	0.9991	1.0	0.9998
273	Pirimicarb	1.0	0.9994	1.0	0.9997	1.0	0.9997	1.0	0.9998
274	Pirimiphos ethyl	1.0	0.9995	1.0	0.9994	1.0	0.9993	1.0	0.9998
275	Pirimiphos methyl	1.0	0.9990	1.0	0.9994	1.0	0.9986	1.0	0.9992
276	Pretilachlor	1.0	0.9986	1.0	0.9999	2.5	0.9994	1.0	0.9998
277	Prochloraz	25.0	0.9960	10.0	0.9960	10.0	0.9984	5.0	0.9976
278	Procymidone	1.0	0.9996	1.0	0.9996	1.0	0.9995	1.0	0.9997
279	Profenofos	1.0	0.9991	1.0	0.9997	1.0	0.9964	1.0	0.9990
280	Profluralin	1.0	0.9991	1.0	0.9940	1.0	0.9980	1.0	0.9942
281	Promecarb	2.5	0.9982	25.0	0.9990	2.5	0.9994	2.5	0.9938
282	Prometon	2.5	0.9996	1.0	0.9991	2.5	0.9993	1.0	0.9999
283	Prometryn	1.0	0.9991	1.0	1.0000	1.0	0.9995	1.0	0.9993
284	Propachlor	1.0	0.9981	1.0	0.9992	1.0	0.9995	1.0	0.9993
285	Propanil	2.5	0.9938	1.0	0.9994	1.0	0.9998	1.0	0.9953
286	Propaquizafop	1.0	0.9994	1.0	0.9990	1.0	0.9994	1.0	0.9991

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
287	Propargite	25.0	0.9964	10.0	0.9987	25.0	0.9868	10.0	0.9995
288	Propazine	1.0	0.9996	10.0	0.9995	2.5	0.9991	2.5	0.9998
289	Propetamphos	1.0	0.9994	2.5	0.9996	1.0	0.9986	1.0	0.9983
290	Propham	1.0	0.9971	1.0	0.9959	1.0	0.9999	1.0	1.0000
291	Propiconazole	2.5	0.9991	1.0	0.9997	1.0	0.9995	1.0	0.9999
292	Propisochlor	1.0	0.9989	10.0	0.9982	1.0	0.9994	2.5	0.9996
293	Propyzamide	1.0	0.9997	1.0	0.9997	1.0	0.9998	1.0	0.9996
294	Prosulfocarb	1.0	0.9994	1.0	0.9997	1.0	0.9996	1.0	0.9993
295	Prothiofos	2.5	0.9980	1.0	0.9999	2.5	0.9995	1.0	0.9997
296	Pyracarbolid	1.0	0.9995	1.0	0.9992	1.0	0.9994	1.0	0.9997
297	Pyraclofos	2.5	0.9998	5.0	0.9991	1.0	0.9989	1.0	0.9984
298	Pyraclostrobin	10.0	0.9982	25.0	0.9984	10.0	0.9999	5.0	0.9982
299	Pyrazophos	1.0	0.9994	2.5	0.9993	1.0	0.9995	1.0	0.9997
300	Pyributicarb	2.5	0.9995	1.0	0.9998	1.0	0.9992	1.0	0.9999
301	Pyridaben	2.5	0.9992	2.5	0.9975	1.0	0.9989	1.0	0.9988
302	Pyridalyl	1.0	0.9995	1.0	0.9993	1.0	0.9995	1.0	0.9991
303	Pyridaphenthion	1.0	0.9993	1.0	0.9996	1.0	0.9995	1.0	0.9999
304	Pyrifenox	1.0	0.9994	1.0	0.9995	1.0	0.9992	1.0	0.9999
305	Pyrimethanil	1.0	0.9985	1.0	0.9989	1.0	0.9989	1.0	0.9943
306	Pyrimidifen	1.0	0.9990	1.0	0.9998	1.0	0.9992	1.0	0.9999
307	Pyriminobac-methyl (E)	1.0	0.9996	1.0	0.9998	1.0	0.9995	1.0	0.9999
308	Pyriminobac-methyl (Z)	1.0	0.9995	1.0	0.9995	1.0	0.9994	1.0	0.9999
309	Pyriproxyfen	2.5	0.9993	1.0	0.9991	1.0	0.9999	2.5	0.9994
310	Pyroquilon	2.5	0.9994	25.0	0.9995	2.5	0.9991	2.5	0.9993
311	Quinalphos	2.5	0.9990	5.0	0.9996	2.5	0.9994	1.0	0.9999
312	Quinoxyfen	1.0	0.9991	1.0	0.9999	1.0	0.9992	1.0	0.9998
313	Quintozene	1.0	0.9990	1.0	0.9986	1.0	0.9987	1.0	0.9985
314	Quizalofop-ethyl	1.0	0.9997	1.0	0.9998	1.0	0.9995	1.0	0.9998
315	Resmethrin	2.5	0.9995	5.0	0.9995	5.0	0.9993	2.5	0.9996

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
316	Secbumeton	10.0	0.9936	1.0	0.9989	5.0	0.9991	2.5	0.9993
317	Silafluofen	1.0	0.9992	1.0	0.9994	1.0	0.9993	1.0	0.9999
318	Simazine	2.5	0.9999	5.0	0.9994	2.5	0.9985	2.5	0.9992
319	Simeconazole	1.0	0.9999	1.0	0.9993	1.0	0.9993	1.0	0.9998
320	Simetryn	2.5	0.9996	1.0	0.9994	5.0	0.9979	2.5	0.9992
321	Spirodiclofen	2.5	0.9947	2.5	0.9997	5.0	0.9982	1.0	0.9956
322	Spiromesifen	1.0	0.9992	1.0	0.9999	1.0	0.9997	1.0	0.9988
323	Sulfotep	1.0	0.9993	1.0	0.9980	1.0	0.9990	1.0	0.9998
324	Sulprofos	1.0	0.9993	1.0	0.9997	1.0	0.9990	1.0	0.9993
325	Tebuconazole	1.0	0.9993	1.0	0.9999	1.0	0.9995	1.0	0.9999
326	Tebufenpyrad	1.0	0.9994	1.0	0.9999	1.0	0.9997	1.0	0.9995
327	Tebupirimfos	1.0	0.9982	1.0	0.9998	1.0	0.9994	1.0	0.9999
328	Tecnazene	1.0	0.9967	1.0	0.9956	1.0	0.9999	1.0	0.9985
329	Tefluthrin	1.0	0.9997	1.0	0.9996	1.0	0.9995	1.0	0.9998
330	Tepraloxydim	25.0	0.9908	10.0	0.9953	10.0	0.9834	10.0	0.9985
331	Terbacil	2.5	0.9994	1.0	1.0000	2.5	0.9984	5.0	0.9996
332	Terbufos	1.0	0.9987	1.0	0.9988	1.0	0.9998	1.0	0.9998
333	Terbumeton	2.5	0.9995	2.5	0.9997	2.5	0.9984	1.0	0.9989
334	Terbuthylazine	1.0	0.9993	1.0	0.9988	2.5	0.9995	1.0	0.9999
335	Terbutryn	1.0	0.9991	1.0	0.9993	1.0	0.9937	1.0	0.9999
336	Tetrachlorvinphos	1.0	0.9983	1.0	0.9989	1.0	0.9981	1.0	0.9985
337	Tetraconazole	1.0	0.9998	1.0	0.9992	1.0	0.9995	1.0	0.9998
338	Tetradifon	1.0	0.9991	1.0	0.9994	1.0	0.9997	1.0	0.9995
339	Thenylchlor	5.0	0.9990	2.5	0.9995	2.5	0.9993	2.5	1.0000
340	Thiazopyr	1.0	0.9996	1.0	0.9993	1.0	0.9994	2.5	0.9995
341	Thifluzamide	1.0	0.9988	1.0	0.9994	1.0	0.9990	1.0	0.9998
342	Thiobencarb	1.0	0.9994	1.0	0.9999	2.5	0.9995	1.0	0.9999
343	Thiometon	2.5	0.9988	5.0	0.9986	1.0	0.9990	1.0	0.9996
344	Tolclofos-methyl	2.5	0.9980	1.0	0.9999	2.5	0.9996	2.5	0.9989

no.	Compounds	Brown rice		Orange		Spinach		Potato	
		LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2	LOQ (μg/kg)	r^2
345	Tolfenpyrad	25.0	0.3295	50.0	0.0208	25.0	0.9953	-	1.0000
346	Tolylfluanid	2.5	0.9959	2.5	0.9917	2.5	0.9914	1.0	0.9966
347	Triadimefon	2.5	0.9993	1.0	0.9993	2.5	0.9983	1.0	0.9991
348	Triadimenol	2.5	0.9998	1.0	0.9997	2.5	0.9930	10.0	0.9991
349	Tri-allate	1.0	0.9985	1.0	0.9995	1.0	0.9997	1.0	0.9997
350	Triazophos	1.0	0.9986	1.0	0.9997	2.5	0.9993	1.0	1.0000
351	Tribufos	2.5	0.9995	1.0	0.9996	2.5	0.9985	1.0	0.9996
352	Tricyclazole	5.0	0.9926	25.0	0.9965	10.0	0.9982	-	0.4717
353	Trifloxystrobin	1.0	0.9994	2.5	0.9995	1.0	0.9991	2.5	0.9996
354	Triflumizole	1.0	0.9990	1.0	0.9987	1.0	0.9994	1.0	0.9996
355	Trifluralin	1.0	0.9984	1.0	0.9985	1.0	0.9989	1.0	0.9999
356	Triticonazole	1.0	0.9996	1.0	0.9994	1.0	0.9999	1.0	0.9985
357	Uniconazole	2.5	0.9990	2.5	0.9996	1.0	0.9996	1.0	0.9997
358	Vernolate	10.0	0.9943	10.0	0.9901	25.0	0.9996	25.0	0.9979
359	Vinclozolin	1.0	0.9997	1.0	0.9981	1.0	0.9985	1.0	0.9984
360	Zoxamide	2.5	0.9989	2.5	0.997	1.0	0.9985	1.0	0.9144

Table S3. Validation data with recoveries (average and relative standard deviations, RSD) and matrix effects (MEs) of 360 target analytes in each crop (brown rice, orange, spinach, and potato)

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
1	2,6-Diisopropylnaphthalene	45.3 (34.8)	81.6 (4.9)	52	103.1 (5.1)	96.7 (5.5)	49	97.8 (5.2)	96.1 (4.5)	50	92.0 (4.0)	98.5 (5.7)	7
2	Acetochlor	101.7 (6.7)	99.0 (2.7)	75	109.1 (3.9)	102.3 (3.4)	65	105.0 (5.3)	103.3 (3.9)	62	112.6 (4.0)	102.3 (2.9)	32
3	Acibenzolar-S-methyl	100.7 (9.0)	91.1 (11.9)	264	64.5 (27.5)	90.4 (9.3)	212	68.3 (9.7)	46.7 (25.8)	196	98.1 (4.1)	87.4 (13.6)	130
4	Acrinathrin	90.8 (7.1)	94.0 (2.2)	402	109.6 (3.9)	105.5 (3.1)	433	101.9 (3.3)	94.8 (3.9)	404	84.9 (7.1)	82.9 (6.2)	121
5	Alachlor	107.5 (4.6)	102.4 (1.0)	61	106.7 (4.9)	101.0 (3.1)	54	104.1 (4.4)	103.8 (4.1)	51	95.7 (3.5)	103.6 (4.1)	22
6	Aldrin	98.2 (14.5)	87.1 (2.2)	34	108.0 (7.4)	96.6 (3.4)	29	103.4 (7.0)	102.6 (5.1)	24	95.2 (8.2)	101.2 (4.1)	5
7	Allidochlor	106.6 (6.8)	100.4 (3.8)	53	108.1 (2.6)	101.0 (4.6)	48	112.0 (3.0)	100.9 (4.9)	46	96.1 (2.8)	108.4 (6.9)	13
8	Ametoctradin	121.6 (9.8)	85.9 (7.0)	>500	96.1 (11.6)	92.8 (3.3)	>500	104.2 (6.2)	91.4 (1.6)	467	93.5 (25.1)	80.2 (3.6)	219
9	Ametryn	103.5 (9.3)	98.6 (1.9)	62	109.5 (5.1)	100.7 (2.1)	50	107.0 (5.4)	91.1 (12.1)	51	91.6 (5.5)	100.4 (2.8)	25
10	Anilofos	84.8 (5.5)	88.8 (2.2)	330	107.1 (2.9)	104.9 (2.1)	216	99.0 (5.3)	92.6 (3.0)	257	98.0 (3.3)	75.2 (1.7)	167
11	Atrazine	103.5 10.0)	99.4 (3.8)	102	105.4 (5.5)	98.3 (3.3)	90	101.3 (2.8)	102.2 (5.2)	86	95.6 (4.1)	99.9 (3.1)	56
12	Azaconazole	101.0 (3.7)	101.0 (1.5)	48	105.2 (4.4)	99.4 (1.5)	49	107.9 (3.7)	101.8 (3.0)	41	96.1 (4.7)	100.7 (2.4)	28
13	Azinphos-ethyl	98.7 (3.5)	94.6 (1.9)	350	101.5 (3.7)	96.5 (2.3)	286	97.5 (4.3)	93.5 (2.1)	267	85.5 (5.3)	78.9 (2.3)	156
14	Azinphos-methyl	82.8 (6.3)	74.7 (5.2)	439	140.8 (2.2)	111.2 (9.9)	57	68.7 (10.4)	79.9 (9.3)	164	52.7 (51.8)	29.6 (14.0)	-14
15	Azoxystrobin	100.9 (3.7)	101.5 (0.8)	228	108.3 (4.4)	100.7 (2.0)	205	101.3 (3.0)	101.6 (3.0)	199	83.6 (4.9)	92.8 (3.6)	81
16	Benalaxyl	101.1 (3.2)	104.3 (1.2)	54	108.9 (4.6)	100.7 (2.4)	48	107.4 (4.3)	103.8 (4.0)	48	95.2 (3.8)	103.5 (2.0)	24
17	Bendiocarb	64.0 (11.6)	85.5 (6.6)	>500	118.2 (4.3)	114.4 (2.4)	>500	89.4 (11.9)	85.2 (7.2)	>500	97.6 (10.9)	102.1 (7.6)	416
18	Benfuresate	103.9 (9.6)	102.2 (3.2)	74	98.4 (7.9)	106.3 (2.9)	58	109.8 (4.0)	104.4 (5.4)	62	92.3 (3.9)	103.5 (3.7)	37
19	Benodanil	101.2 (4.7)	99.0 (2.0)	>500	122.3 (3.5)	105.7 (2.8)	>500	105.0 (4.6)	102.5 (3.2)	>500	91.5 (1.7)	90.4 (3.3)	>500
20	Benthiavalicarb-isopropyl	102.2 (6.5)	100.7 (2.3)	166	107.8 (3.8)	99.0 (3.8)	186	104.4 (3.4)	102.6 (3.6)	163	90.5 (7.6)	96.7 (2.1)	126
21	Benzoylprop-ethyl	104.0 (1.4)	102.5 (1.6)	53	107.2 (4.4)	101.9 (2.7)	47	104.0 (6.3)	104.9 (3.5)	45	96.8 (4.2)	102.5 (1.4)	19
22	BHC, *α*-	107.6 (4.5)	97.9 (2.2)	75	110.9 (4.5)	100.7 (2.0)	74	106.9 (3.5)	101.4 (3.8)	63	97.4 (3.7)	101.3 (6.7)	34
23	BHC, *β*-	103.8 (3.7)	98.5 (3.1)	57	109.8 (5.5)	100.3 (2.6)	60	104.0 (2.2)	94.9 (2.4)	30	94.8 (6.2)	99.9 (4.1)	32
24	BHC, *δ*-	90.5 (3.4)	90.8 (2.8)	162	106.7 (4.5)	103.1 (1.8)	124	104.2 (3.0)	96.6 (1.7)	91	93.6 (5.3)	82.6 (3.8)	53
25	BHC, *γ*-	101.5 (6.0)	103.7 (3.8)	60	107.8 (6.9)	99.2 (2.5)	63	105.2 (4.2)	99.5 (3.4)	39	93.4 (2.7)	100.7 (2.0)	41
26	Bifenazate	90.2 (4.6)	83.0 (1.9)	245	102.5 (4.0)	98.9 (2.0)	227	95.0 (4.7)	78.8 (3.3)	206	27.1 (11.7)	73.9 (5.4)	133
27	Bifenox	102.7 (7.3)	94.0 (4.9)	399	101.2 (6.1)	94.8 (2.9)	351	94.1 (4.8)	93.1 (3.2)	339	83.5 (30.3)	69.0 (3.9)	137
28	Bifenthrin	95.8 (2.4)	97.0 (1.4)	61	109.3 (2.3)	101.5 (3.1)	57	99.0 (4.6)	101.8 (2.7)	56	95.0 (2.3)	101.9 (2.2)	36
29	Binapacryl	N.D	N.D	>500	N.D	N.D	>500	N.D	N.D	>500	N.D	N.D	>500
30	Bitertanol	102.4 (3.4)	99.4 (1.3)	110	104.5 (2.5)	98.0 (2.4)	148	108.6 (4.1)	101.6 (3.2)	123	88.0 (3.4)	96.0 (1.5)	68
31	Bixafen	97.5 (8.1)	101.4 (1.7)	127	105.0 (2.0)	101.9 (3.7)	125	107.4 (2.2)	101.8 (1.9)	115	93.4 (3.0)	99.5 (2.1)	65

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
32	Boscalid	100.8 (2.8)	100.0 (0.4)	135	107.1 (2.8)	100 (2.2)	150	105.5 (2.8)	102.6 (3.2)	130	92.2 (3.7)	97.7 (1.8)	75
33	Bromacil	97.8 (8.1)	77.0 (8.0)	>500	101.7 (6.8)	94.5 (6.5)	>500	N.D	100.6 (4.8)	>500	94.1 (10.9)	99.3 (6.4)	439
34	Bromobutide	101.1 (12.9)	103.1 (2.1)	69	110.2 (8.2)	102.7 (2.1)	63	103.4 (5.3)	102.7 (3.3)	60	82.1 (5.4)	100.8 (2.6)	33
35	Bromophos	96.3 (4.2)	96.8 (2.3)	109	105.8 (7.9)	102.3 (3.3)	86	103.2 (1.8)	98.9 (2.1)	88	94.5 (6.0)	97.3 (1.9)	54
36	Bromopropylate	98.0 (2.9)	99.6 (1.6)	79	108.1 (4.0)	101.7 (3.2)	73	107.2 (3.6)	103.1 (3.1)	72	94.7 (2.5)	100.4 (1.4)	44
37	Bupirimate	121.9 (3.6)	104.1 (1.7)	108	110.8 (6.1)	102.5 (3.1)	98	108.4 (5.0)	111.7 (1.9)	97	98.5 (3.7)	102.7 (2.2)	75
38	Buprofezin	108.7 (6.0)	96.4 (3.5)	45	112.2 (4.8)	100.3 (4.5)	47	104.7 (4.8)	101.8 (1.8)	33	100.4 (2.4)	101.9 (1.5)	24
39	Butachlor	104.5 (2.6)	98.4 (1.1)	64	106.6 (3.2)	102 (2.5)	56	103.2 (2.8)	102.5 (2.4)	52	94.9 (3.0)	102.3 (2.1)	27
40	Butafenacil	102.8 (1.7)	103.1 (0.8)	158	108.1 (3.8)	101.7 (2.0)	135	107.5 (3.8)	104.0 (3.2)	138	86.4 (1.8)	91.5 (1.4)	46
41	Butralin	109.1 (3.0)	93.3 (3.5)	99	102.0 (5.7)	95.9 (1.9)	77	102.5 (4.8)	97.1 (4.2)	84	86.5 (7.9)	86.1 (2.9)	32
42	Butylate	113.7 (7.8)	101.8 (4.7)	34	111.9 (4.9)	100.1 (3.9)	21	109.7 (3.2)	96.8 (5.4)	30	96.6 (4.9)	106.1 (7.6)	0
43	Cadusafos	104.1 (4.1)	99.2 (2.0)	73	108.0 (2.2)	100.2 (3.0)	68	109.8 (4.6)	100.0 (3.1)	63	92.5 (3.1)	106.6 (4.9)	28
44	Cafenstrole	N.D	42.1 (16.0)	>500	132.0 (4.8)	132.1 (4.0)	>500	69.4 (13.2)	74.1 (9.3)	>500	88.4 (16.2)	48.7 (14.5)	473
45	Captafol	N.D	N.D	-	N.D	N.D	-	N.D	N.D	-	N.D	N.D	-
46	Captan	N.D	N.D	-	N.D	N.D	-	N.D	N.D	-	N.D	N.D	-
47	Carbaryl	35.3 (15.9)	61.1 (6.1)	>500	142.3 (7.7)	125.6 (6.8)	>500	68.4 (22.1)	77.4 (8.7)	>500	74.0 (16.0)	1.9 (55.4)	>500
48	Carbofuran	80.3 (8.8)	81.9 (3.8)	>500	105.7 (4.0)	103.8 (6.4)	>500	76.6 (8.0)	92.4 (6.7)	>500	116.4 (12.9)	112.8 (12.0)	239
49	Carbophenothion	103.4 (2.2)	96.1 (3.1)	94	109.9 (4.7)	102.0 (2.2)	78	102.7 (4.5)	99.7 (3.7)	79	96.4 (4.8)	93.9 (1.8)	38
50	Carbosulfan	N.D	104.7 (7.5)	-93	11.2 (29.5)	N.D	23	139.8 (18.4)	142.2 (12.3)	-85	76.5 (8.6)	74.9 (3.2)	68
51	Carboxin	100.2 (6.0)	93.1 (2.2)	259	103.6 (4.3)	98.2 (2.2)	256	106.5 (5.0)	101.1 (2.4)	232	95.6 (2.3)	99.4 (2.8)	161
52	Chinomethionat	61.9 (7.5)	60.3 (4.0)	497	87.3 (3.0)	91.3 (4.2)	403	74.8 (3.5)	74.3 (6.6)	423	72.9 (7.0)	40.8 (20.9)	114
53	Chlordane-cis	95.7 (6.8)	93.5 (3.4)	0	104.8 (5.1)	99.4 (7.1)	25	102.1 (9.6)	101.4 (4.4)	10	98.4 (9.7)	98.7 (2.6)	8
54	Chlordane-trans	100.5 (2.8)	97.3 (3.0)	35	106.3 (5.5)	100.8 (4.0)	29	94.9 (5.4)	98.4 (5.1)	29	93.5 (5.3)	102.7 (2.9)	8
55	Chlorethoxyfos	109.4 (8.7)	102.8 (4.1)	41	109.8 (1.3)	99.2 (3.4)	41	101.6 (11.1)	91.8 (4.7)	15	92.3 (3.6)	101.9 (6.8)	11
56	Chlorfenapyr	92.6 (12.7)	102.4 (7.1)	35	98.1 (7.8)	100.4 (9.3)	35	104.4 (6.9)	99.7 (10.1)	30	91.4 (8.0)	100.7 (4.9)	18
57	Chlorfenson	107.8 (2.4)	106.9 (3.1)	-30	110.9 (4.6)	101.2 (2.9)	113	108.3 (4.6)	103.7 (4.0)	93	96.7 (2.6)	100.9 (2.5)	64
58	Chlorfenvinphos	91.3 (3.6)	96.6 (1.2)	96	106.6 (3.5)	101.4 (0.8)	98	101.4 (3.4)	96.3 (1.8)	86	77.6 (49.1)	97.7 (3.1)	65
59	Chlorfluazuron	108.9 (5.3)	98.7 (9.6)	155	105.9 (3.3)	100.6 (5.2)	184	106.2 (8.5)	102.5 (4.0)	161	88.9 (1.8)	101.1 (7.6)	105
60	Chlorflurenol-methyl	102.8 (4.7)	102.7 (3.1)	94	109.3 (7.7)	101.5 (1.4)	85	107.8 (4.6)	102.7 (3.8)	83	102.4 (6.3)	101.7 (3.9)	53
61	Chlorobenzilate and chloropropylate	102.3 (2.2)	98.9 (1.5)	69	107.7 (3.0)	101.9 (3.1)	61	108.4 (5.0)	103.6 (3.0)	57	96.8 (2.2)	103.2 (1.7)	32
62	Chloroneb	121.4 (9.4)	104.6 (4.0)	51	107.2 (2.7)	98.4 (2.9)	39	129.9 (9.7)	104.7 (5.7)	44	94.8 (2.8)	107.2 (7.4)	13
63	Chlorothalonil	45.5 (6.6)	18.8 (7.6)	>500	96.1 (5.0)	100.5 (16.3)	>500	60.1 (10.6)	34.7 (24.8)	>500	89.8 (61.6)	40.1 (16.5)	>500
64	Chlorpropham	107.5 (3.6)	92.6 (7.5)	141	102.3 (5.9)	102.8 (2.8)	176	111.0 (3.7)	102.1 (2.8)	151	98.1 (2.6)	108.4 (2.3)	90
65	Chlorpyrifos	99.7 (1.8)	100.3 (2.1)	60	109.5 (4.1)	102.2 (3.8)	52	105.4 (5.4)	101.3 (4.2)	51	99.8 (5.4)	100.6 (1.8)	29
66	Chlorpyrifos-methyl	96.3 (5.8)	97.6 (1.4)	110	108.0 (5.2)	100.9 (2.0)	99	99.8 (3.2)	98.6 (4.1)	98	95.5 (5.0)	96.5 (2.0)	61

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
67	Chlorthal-dimethyl	100.6 (6.2)	101.6 (2.2)	42	110.7 (4.9)	101.9 (2.6)	35	108.3 (4.4)	102.3 (5.4)	33	95.2 (3.6)	102.8 (2.0)	20
68	Chlorthiophos	101.2 (4.5)	98.5 (1.5)	62	109.6 (4.7)	102.0 (2.7)	54	103.2 (2.9)	99.8 (3.4)	53	95.8 (3.9)	99.0 (1.6)	27
69	Chlozolinate	101.9 (4.5)	99.5 (5.2)	53	111.5 (4.9)	103.0 (3.0)	44	103.9 (5.4)	94.2 (2.5)	39	64.9 (6.1)	95.0 (2.8)	25
70	Cinmethylin	112.4 (6.1)	99.1 (3.2)	57	99.8 (15.7)	100.3 (7.9)	41	72.5 (8.6)	101.4 (4.1)	41	91.7 (10.7)	102.9 (2.1)	26
71	Clomazone	105.0 (5.1)	103.0 (1.6)	113	105.1 (4.1)	99 (1.3)	115	102.9 (2.8)	100.2 (2.6)	82	95.3 (2.1)	104.1 (1.5)	53
72	Clomeprop	101.0 (5.5)	100.0 (1.9)	91	105.3 (6.4)	102 (3.5)	89	106.4 (4.1)	101.1 (3.2)	85	95.7 (2.3)	99.5 (1.5)	41
73	Coumaphos	97.7 (3.1)	94.7 (2.7)	395	110.1 (2.1)	100.4 (2.0)	328	97.0 (3.6)	96.6 (1.6)	308	88.4 (5.0)	77.5 (6.7)	141
74	Cyanazine	N.D	82.0 (6.1)	79	104.3 (5.8)	100.7 (10.0)	165	134.8 (9.1)	101.5 (29.4)	64	37.5 (4.6)	85.9 (10.5)	214
75	Cyanophos	94.9 (6.0)	101.1 (1.1)	137	108.3 (4.4)	101.9 (2.0)	124	106.0 (3.9)	100.4 (2.4)	123	94.3 (2.3)	99.6 (2.1)	71
76	Cycloate	110.0 (8.7)	101.1 (2.9)	49	113.3 (5.0)	99.8 (3.2)	36	108.6 (3.1)	99.9 (4.9)	43	92.0 (2.7)	107.0 (6.1)	4
77	Cyflufenamid	101.1 (8.6)	106.7 (8.7)	47	115.1 (14.1)	101.5 (2.2)	46	102.6 (11.3)	103.6 (10.0)	47	87.3 (16.5)	105.7 (7.4)	22
78	Cyflumetofen	N.D	55.5 (7.5)	483	132.0 (2.2)	129 (6.7)	>500	89.8 (10.9)	95.3 (4.9)	>500	118.0 (7.8)	72.8 (12.7)	332
79	Cyfluthrin	89.5 (5.3)	92.1 (2.4)	320	108.3 (2.8)	103.3 (2.6)	311	103.2 (3.2)	98.1 (1.6)	281	86.1 (1.8)	81.4 (4.6)	125
80	Cyhalofop-butyl	101.8 (3.4)	102.2 (1.1)	143	109.8 (4.0)	102.4 (2.1)	128	106.1 (4.4)	103.0 (3.3)	127	75.0 (3.2)	90.3 (2.2)	72
81	Cyhalothrin	99.2 (3.0)	97.0 (1.2)	159	108.7 (9.4)	99.5 (2.6)	141	106.5 (4.5)	110.3 (4.5)	141	85.6 (3.0)	90.5 (3.7)	54
82	Cypermethrin	90.7 (2.8)	92.3 (2.0)	376	112.6 (3.1)	106.2 (2.8)	373	106.2 (2.4)	94.4 (2.2)	347	83.1 (3.5)	79.5 (4.9)	113
83	Cyproconazole	99.1 (2.4)	102.5 (1.1)	133	101.8 (4.8)	100.6 (2.7)	133	108.1 (4.0)	100.1 (2.5)	123	91.7 (3.8)	104.9 (4.0)	17
84	Cyprodinil	96.7 (2.6)	95.4 (3.3)	63	105.8 (3.4)	99.6 (2.5)	54	103.8 (4.1)	101.7 (3.7)	53	96.3 (5.8)	104.0 (3.3)	24
85	DDD, o, p'-	91.3 (3.5)	92.0 (1.2)	55	107.0 (2.8)	99.0 (3.8)	36	102.0 (4.4)	107.0 (3.6)	38	96.0 (2.5)	102.7 (1.1)	0
86	DDD, p, p'-	92.9 (3.0)	92.2 (1.3)	105	102.2 (4.5)	97.7 (3.0)	70	100.7 (6.5)	104.2 (3.9)	69	95.1 (2.3)	96.4 (2.0)	11
87	DDE, o, p'-	93.3 (1.8)	92.0 (1.2)	37	108.0 (4.0)	101.0 (3.2)	31	102.2 (4.5)	99.8 (3.5)	30	96.4 (3.7)	102.6 (1.4)	12
88	DDE, p, p'-	91.3 (2.5)	88.1 (2.1)	25	105.2 (2.2)	99.0 (4.4)	28	99.9 (3.1)	99.3 (3.4)	22	97.0 (3.7)	103.7 (1.4)	11
89	DDT, o, p'-	116.3 (5.7)	108.7 (4.3)	-22	115.0 (2.6)	104.9 (3.1)	14	350.0 (107)	74.1 (4.5)	-40	91.0 (3.4)	96.0 (2.0)	43
90	DDT, p, p'-	116.7 (6.8)	103.8 (2.3)	-3	125.9 (2.7)	115 (2.3)	58	105.3 (7.3)	67.9 (6.2)	-27	92.5 (4.3)	88.3 (1.8)	118
91	Deltamethrin	82.4 (3.5)	78.1 (2.2)	318	108.6 (3.3)	106.6 (2.1)	411	97.5 (4.1)	86.5 (1.9)	345	85.3 (5.1)	77.4 (6.9)	62
92	Desmetryn	100.0 (6.9)	100.2 (1.7)	70	104.7 (1.9)	96.9 (2.2)	63	104.2 (4.1)	100.9 (4.8)	57	92.8 (5.1)	103.4 (2.6)	27
93	Di-Allate	109.6 (7.0)	102.0 (3.5)	53	112.2 (4.4)	99.9 (3.2)	40	111.9 (4.7)	100.3 (3.3)	48	92.2 (2.4)	105.1 (4.4)	12
94	Diazinon	106.4 (7.0)	100.3 (3.0)	62	108.8 (4.0)	99.5 (2.4)	58	114.1 (7.2)	102.9 (5.6)	50	96.5 (7.5)	105.1 (3.7)	23
95	Dichlobenil	113.2 (5.8)	104.2 (3.5)	37	106.0 (2.6)	97.4 (3.2)	32	114.9 (2.7)	103.4 (5.4)	30	96.2 (2.7)	109.5 (6.4)	-1
96	Dichlofenthion	103.1 (2.9)	99.0 (2.3)	63	107.7 (3.2)	101.5 (3.0)	52	105.1 (4.5)	102.7 (2.6)	52	93.0 (2.4)	100.5 (2.8)	25
97	Dichlofluanid	58.1 (8.4)	16.2 (4.2)	>500	115.5 (4.2)	80.1 (4.8)	>500	63.1 (13.5)	11.2 (7.1)	>500	117.7 (9.1)	61.3 (9.5)	>500
98	Dichlormid	109.2 (7.3)	104.0 (4.6)	44	112.9 (3.1)	100.2 (3.2)	40	108.2 (4.5)	100.6 (4.2)	32	97.0 (3.6)	108.0 (6.7)	7
99	Dichlorvos	78.3 (7.9)	86.2 (4.2)	65	108.6 (2.4)	96.4 (3.6)	70	97.8 (3.2)	81.7 (8.9)	58	92.2 (2.9)	102.8 (7.6)	29
100	Diclofop-methyl	96.5 (4.7)	98.8 (1.1)	90	108.5 (4.0)	101.6 (2.4)	81	104.9 (5.2)	100.6 (2.8)	77	54.5 (4.6)	81.3 (4.9)	40
101	Dicloran	102.0 (13.6)	102.5 (5.3)	100	81.0 (6.8)	85.5 (12.4)	123	105.5 (9.0)	100.1 (4.4)	110	90.5 (5.3)	92.2 (3.8)	26
102	Dicofol	103.1 (9.1)	95.0 (3.8)	76	103.4 (9.6)	101.9 (4.0)	63	103.7 (3.7)	100.0 (4.3)	64	95.3 (3.6)	103.4 (3.0)	40

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
103	Dicrotophos	85.8 (14.0)	88.9 (6.5)	>500	107.7 (8.0)	95.7 (3.3)	419	81.9 (8.5)	72.4 (11.1)	339	91.7 (6.3)	74.2 (10.1)	279
104	Dieldrin	102.5 (19.3)	93.1 (2.4)	30	114.6 (6.9)	101.7 (5.5)	34	112.0 (7.7)	98.7 (3.5)	25	96.0 (7.9)	100.8 (6.3)	12
105	Diethatyl-ethyl	97.5 (6.6)	105.4 (2.6)	18	108.7 (4.3)	99.4 (5.9)	50	109.2 (4.9)	101.5 (2.1)	29	96.7 (7.1)	100.7 (2.3)	28
106	Diethofencarb	95.0 (7.0)	100.6 (3.1)	86	106.7 (5.0)	101.2 (2.3)	75	110.2 (3.8)	103.4 (4.3)	73	93.7 (3.9)	104.1 (3.1)	43
107	Difenoconazole	100.1 (1.4)	100.0 (0.8)	269	108.3 (3.5)	100.5 (3.2)	253	104.7 (2.0)	99.0 (3.0)	237	88.0 (4.6)	96.7 (2.3)	158
108	Diflufenican	102.8 (4.3)	101.3 (1.5)	78	109.2 (4.4)	103.1 (2.8)	68	105.9 (3.8)	103.4 (3.5)	69	94.3 (4.8)	100.0 (2.5)	35
109	Dimepiperate	99.1 (2.4)	98.0 (1.4)	84	106.5 (3.5)	100.5 (2.0)	77	105.0 (5.1)	101.7 (3.2)	64	91.0 (2.2)	99.4 (1.0)	48
110	Dimethachlor	102.0 (4.4)	98.8 (2.4)	65	113.0 (1.9)	98.9 (9.5)	44	106.9 (6.3)	100.7 (2.8)	45	95.9 (3.4)	101.3 (2.0)	31
111	Dimethametryn	100.8 (3.9)	98.2 (2.3)	52	106.3 (3.9)	100.3 (2.4)	45	106.4 (4.4)	102.1 (16.7)	43	96.3 (3.1)	104.0 (1.8)	20
112	Dimethenamid	102.7 (1.8)	101.7 (1.0)	57	105.1 (1.2)	101.5 (2.8)	48	109.5 (3.4)	101.7 (2.2)	44	94.7 (2.6)	101.4 (1.7)	26
113	Dimethipin	84.5 (13.3)	85.6 (4.0)	>500	113.5 (6.8)	102.8 (6.5)	>500	89.1 (6.5)	96.0 (5.2)	>500	93.5 (24.6)	90.6 (8.6)	162
114	Dimethoate	103.4 (12.8)	97.6 (7.4)	333	104.4 (13.8)	95.1 (5.0)	298	102.4 (17.4)	98.1 (5.3)	231	107.0 (29.4)	85.6 (8.2)	202
115	Dimethomorph	98.9 (1.9)	101.4 (1.6)	127	104.9 (4.3)	99.5 (2.0)	112	106.8 (3.0)	92.3 (2.8)	100	92.6 (9.5)	96.2 (2.6)	39
116	Dimethylvinphos	81.1 (6.7)	86.3 (3.5)	200	108.3 (4.3)	100.8 (2.7)	214	88.3 (7.1)	80.9 (9.7)	159	100.8 (5.0)	90.3 (2.3)	147
117	Diniconazole	99.5 (4.0)	99.9 (1.0)	79	106.9 (4.9)	100.7 (2.4)	71	105.4 (3.2)	102.5 (3.0)	67	93.2 (4.4)	99.7 (1.2)	37
118	Dinitramine	107.4 (4.7)	98.1 (5.0)	92	110.7 (6.1)	102.3 (2.4)	73	94.7 (15.8)	93.9 (11.6)	78	88.1 (19.2)	91.3 (7.4)	19
119	Dioxathion	108.6 (12.3)	98.2 (5.0)	73	119.6 (10.2)	101.9 (3.3)	26	107.4 (8.8)	104.1 (9.2)	69	88.9 (18.2)	96.5 (3.2)	36
120	Diphenamid	103.1 (3.5)	101.3 (1.2)	51	108.1 (3.4)	102.0 (2.3)	43	107.4 (5.0)	103.7 (3.2)	41	97.1 (4.6)	103.0 (1.8)	25
121	Diphenylamine	97.0 (6.9)	93.4 (5.0)	134	112.3 (6.0)	99.8 (5.8)	194	94.9 (4.3)	97.4 (7.8)	161	90.8 (0.6)	91.4 (9.9)	95
122	Disulfoton	100.1 (4.3)	94.7 (3.2)	79	104.3 (3.8)	101.7 (3.8)	68	102.6 (5.5)	95.3 (5.2)	67	93.8 (2.4)	98.3 (1.9)	34
123	Dithiopyr	102.5 (4.3)	102.1 (1.9)	40	111.9 (3.9)	101.8 (2.2)	31	106.1 (4.1)	105.1 (3.5)	30	94.2 (2.7)	104.2 (1.7)	12
124	Edifenphos	43.2 (9.9)	70.8 (4.9)	240	117.9 (4.7)	108.0 (1.2)	471	80.2 (8.5)	81.8 (6.3)	287	95.4 (3.7)	71.3 (2.4)	272
125	Endosulfan, α-	103.3 (6.0)	102.4 (5.5)	-13	102.2 (7.6)	98.4 (9.8)	25	107.4 (5.7)	104.2 (4.9)	-4	96.6 (7.0)	103.0 (2.3)	11
126	Endosulfan, β-	96.0 (13.9)	100.3 (6.9)	37	120.0 (11.4)	106.1 (5.2)	29	101.8 (13.6)	100.7 (5.3)	23	101.8 (9.9)	103.4 (8.0)	7
127	Endosulfan, sulfate-	93.2 (3.6)	91.7 (0.9)	205	107.0 (2.7)	100.2 (2.0)	134	99.3 (3.2)	96.5 (2.0)	155	98.6 (2.5)	95.3 (2.3)	128
128	Endrin	66.6 (32.6)	89.1 (13.8)	47	112.5 (17.1)	89.6 (15.6)	48	72.9 (40.3)	113.7 (17.6)	13	91.1 (44.1)	89.4 (8.6)	27
129	EPN	99.0 (0.9)	95.0 (2.2)	218	107.1 (3.9)	97.3 (3.2)	175	98.7 (3.5)	96.8 (2.3)	174	88.8 (6.8)	75.8 (8.4)	72
130	Epoxiconazole	101.8 (2.1)	103.0 (0.9)	71	103.4 (4.2)	96.8 (1.7)	70	103.1 (3.4)	100.0 (2.2)	40	91.3 (3.1)	97.2 (1.9)	40
131	EPTC	116.5 (6.6)	100.9 (5.0)	34	110.7 (5.1)	99.5 (4.3)	-1	115.0 (5.0)	100.0 (6.3)	5	93.1 (6.1)	106.9 (7.9)	-2
132	Esprocarb	101.1 (3.7)	102.0 (0.8)	42	109.7 (4.2)	99.0 (6.9)	47	109.9 (5.8)	101.1 (3.3)	37	93.0 (1.9)	104.2 (0.9)	24
133	Etaconazole	98.7 (2.9)	101.5 (1.1)	171	107.9 (4.8)	99.8 (1.8)	175	110.7 (5.0)	101.1 (3.7)	161	96.4 (6.0)	103.0 (2.9)	127
134	Ethalfluralin	105.9 (4.8)	101.6 (2.1)	70	111.0 (6.1)	99.4 (5.0)	62	105.4 (6.0)	105.0 (4.4)	61	88.9 (2.4)	92.4 (5.0)	5
135	Ethiofencarb	46.5 (9.9)	75.6 (4.2)	>500	108.0 (6.7)	117.2 (9.3)	>500	80.8 (11.7)	86.2 (4.0)	>500	118.6 (13.3)	83.2 (11.1)	421
136	Ethion	100.7 (3.0)	99.2 (2.1)	89	108.8 (3.0)	102.6 (1.9)	75	104.3 (4.1)	103.8 (2.6)	73	91.0 (3.3)	97.9 (1.4)	36
137	Ethofumesate	98.5 (8.3)	102.7 (2.2)	51	113.2 (3.6)	100.7 (3.9)	49	109.8 (6.6)	102.7 (3.6)	47	96.3 (5.1)	103.1 (2.8)	26
138	Ethoprophos	105.0 (5.6)	98.7 (5.4)	94	109.4 (4.9)	100.5 (2.9)	82	103.9 (4.1)	100.5 (3.1)	88	93.7 (2.8)	104.6 (3.2)	43

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
139	Ethoxyquin	77.6 (4.4)	58.0 (2.3)	137	109.9 (3.8)	97.4 (3.5)	134	10.3 (34.5)	43.5 (13.8)	109	26.2 (11.8)	102.6 (2.7)	60
140	Etofenprox	101.8 (3.1)	95.6 (0.9)	85	108.4 (3.8)	100.7 (3.4)	71	105.3 (3.2)	102.2 (3.7)	68	94.4 (0.9)	102.4 (2.2)	29
141	Etoxazole	98.5 (6.9)	103.4 (3.1)	58	108.3 (5.2)	100.6 (2.9)	53	105.1 (4.8)	101.2 (3.1)	58	94.9 (2.4)	98.2 (1.3)	30
142	Etridiazole	122.6 (8.1)	110.8 (5.3)	27	115.8 (5.6)	97.0 (3.4)	43	112.5 (6.6)	81.6 (11.2)	-1	92.7 (4.7)	92.3 (9.5)	37
143	Etrimfos	105.1 (4.3)	104.0 (2.3)	83	107.7 (5.5)	99.0 (2.9)	77	107.1 (5.7)	100.2 (5.3)	76	85.2 (6.5)	101.0 (3.7)	36
144	Fenamidone	106.1 (3.3)	102.9 (2.9)	63	107.8 (5.0)	101.4 (2.3)	56	104.3 (5.9)	103.2 (3.5)	52	93.6 (2.6)	99.7 (2.6)	30
145	Fenamiphos	99.1 (8.6)	100.0 (4.0)	388	108.8 (4.3)	100.2 (2.0)	420	83.2 (49.3)	97.6 (2.0)	387	91.6 (3.0)	101.2 (3.8)	264
146	Fenarimol	99.0 (6.1)	99.7 (1.6)	57	107.4 (5.9)	99.2 (1.7)	59	104.4 (3.2)	100.0 (3.7)	51	91.8 (2.5)	98.5 (2.7)	28
147	Fenazaquin	97.8 (4.7)	96.0 (1.1)	66	105.9 (3.1)	100.5 (3.1)	67	99.9 (4.0)	99.8 (2.8)	61	95.7 (2.7)	101.1 (1.7)	30
148	Fenbuconazole	118.7 (2.8)	105.5 (1.3)	103	110.1 (6.1)	101.4 (3.1)	107	109.9 (7.9)	104.1 (2.5)	93	92.0 (7.5)	96.9 (1.8)	48
149	Fenchlorphos	98.3 (3.7)	98.0 (2.7)	87	108.3 (4.5)	101 (2.3)	76	104.9 (3.6)	101.6 (3.2)	68	95.4 (4.2)	97.8 (1.8)	39
150	Fenclorim	104.3 (4.8)	95.6 (2.4)	117	110.2 (4.1)	99.5 (3.1)	128	106.5 (4.1)	99.1 (4.8)	110	93.6 (0.9)	102.5 (2.0)	69
151	Fenfuram	100.0 (8.4)	102.0 (1.2)	144	105.2 (6.0)	98.9 (1.7)	134	105.2 (4.3)	102.9 (3.7)	123	96.2 (2.5)	101.7 (3.2)	73
152	Fenhexamid	102.1 (4.4)	96.3 (3.4)	>500	107.2 (3.4)	101.7 (2.0)	>500	103.8 (4.7)	100.2 (1.5)	>500	129.4 (40.4)	98.2 (1.5)	>500
153	Fenitrothion	104.5 (3.3)	98.8 (2.5)	177	105.9 (3.7)	99.5 (1.4)	143	95.5 (3.7)	98.2 (3.1)	153	88.6 (5.1)	85.4 (4.6)	64
154	Fenobucarb	103.9 (6.3)	95.2 (4.5)	254	93.4 (11.3)	94.8 (2.5)	307	103.1 (5.5)	100.8 (2.9)	285	99.2 (3.8)	107.9 (8.8)	139
155	Fenothiocarb	100.1 (2.4)	101.0 (1.0)	321	106.8 (4.3)	100.1 (2.8)	312	108.9 (4.7)	103.6 (2.7)	304	93.3 (2.4)	103.1 (4.0)	201
156	Fenoxanil	95.6 (3.1)	97.0 (2.3)	>500	110.1 (4.4)	101.9 (3.4)	>500	106.1 (3.9)	103.2 (4.7)	>500	105.5 (4.1)	95.9 (2.5)	>500
157	Fenpiclonil	100.7 (4.0)	88.4 (2.8)	>500	111.4 (4.9)	101.1 (5.9)	>500	46.7 (28.4)	100.5 (2.6)	363	96.1 (6.3)	1.4 (10.0)	130
158	Fenpropathrin	101.0 (7.2)	98.9 (1.3)	92	114.6 (4.2)	103.5 (4.0)	79	105.0 (7.4)	103.6 (4.1)	85	99.5 (7.6)	96.7 (1.8)	37
159	Fenpyrazamine	96.0 (6.7)	97.9 (3.2)	428	111.7 (3.7)	108.2 (2.8)	321	101.7 (7.2)	96.1 (2.6)	340	87.3 (6.6)	84.6 (11.0)	162
160	Fenson	97.5 (3.7)	100.3 (1.6)	87	109.2 (2.9)	102.3 (3.0)	80	106.7 (2.8)	104.3 (3.9)	74	97.3 (3.3)	103.4 (1.6)	53
161	Fensulfothion	107.3 (4.2)	99.2 (1.1)	>500	104.9 (5.6)	97.3 (3.3)	>500	103.4 (3.6)	97.6 (1.2)	>500	81.1 (7.2)	81.3 (3.0)	464
162	Fenthion	100.6 (3.0)	99.2 (1.6)	73	105.7 (3.6)	101.2 (1.6)	61	104.6 (4.6)	100.2 (3.3)	61	98.4 (1.8)	100.1 (2.3)	32
163	Fenvalerate	104.9 (4.3)	94.1 (2.0)	257	108.8 (3.8)	103 (3.7)	274	99.5 (4.4)	94.4 (2.7)	251	84.1 (2.5)	83.2 (4.0)	87
164	Fipronil	105.5 (5.8)	102.4 (2.3)	225	109.0 (4.4)	100.8 (2.9)	195	100.8 (5.0)	101.9 (6.9)	195	92.1 (8.2)	98.1 (1.5)	132
165	Flonicamid	98.6 (7.9)	95.6 (5.3)	361	103.0 (4.4)	98.4 (1.4)	381	106.8 (4.6)	101.3 (3.7)	337	103.3 (3.3)	88.7 (11.4)	182
166	Fluacrypyrim	99.1 (4.2)	102.1 (2.4)	70	109.9 (3.0)	102.6 (3.0)	64	107.6 (5.2)	105.4 (2.5)	58	98.3 (1.5)	104.9 (2.1)	31
167	Fluazifop-butyl	100.5 (2.7)	102.0 (1.8)	75	111.1 (4.6)	104.3 (2.6)	67	108.1 (4.5)	103.2 (1.9)	69	93.9 (1.8)	102.4 (1.9)	38
168	Fluazinam	N.D	76.6 (9.3)	401	104.3 (4.7)	94.9 (11.5)	463	63.7 (44.3)	71.2 (9.3)	243	238.3 (244.9)	6.6 (160.7)	-60
169	Fluchloralin	102.0 (5.5)	97.4 (3.6)	84	108.7 (2.6)	98 (3.5)	70	104.8 (4.6)	99.1 (2.5)	66	86.9 (4.9)	86.4 (4.3)	15
170	Flucythrinate	100.7 (3.0)	96.3 (1.4)	240	107.5 (2.0)	101.8 (3.3)	223	101.8 (4.0)	97.7 (2.2)	220	85.0 (2.3)	83.9 (3.1)	86
171	Fludioxonil	103.6 (17.9)	102.9 (3.2)	>500	108.6 (4.0)	101.5 (3.6)	>500	86.7 (51.9)	103.2 (3.3)	>500	97.3 (2.6)	87.9 (6.7)	>500
172	Flufenacet	75.4 (7.3)	89.0 (2.6)	107	110.7 (5.7)	101.9 (2.3)	149	101.1 (4.1)	96.2 (1.6)	115	93.5 (4.7)	92.7 (9.1)	88
173	Flumetralin	98.6 (3.4)	93.1 (1.9)	94	103.7 (4.3)	98 (1.5)	75	104.5 (3.3)	98.3 (3.3)	72	90.4 (2.3)	89.9 (1.7)	36
174	Flumiclorac-pentyl	98.2 (2.2)	101.0 (1.2)	183	110.9 (4.0)	102.7 (2.8)	164	103.7 (1.5)	97.5 (3.0)	164	71.6 (5.1)	83.4 (4.6)	56

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
175	Flumioxazin	105.8 (5.8)	100.5 (2.0)	333	108.2 (5.0)	98.7 (2.7)	249	84.2 (49.8)	97.8 (2.9)	286	82.7 (8.5)	80.4 (3.8)	55
176	Fluopicolide	100.2 (3.2)	100.1 (2.1)	115	106.4 (2.1)	101.5 (3.0)	109	107.1 (5.7)	103.2 (3.5)	99	95.4 (4.3)	101.2 (2.8)	67
177	Fluopyram	103.5 (2.3)	100.9 (1.9)	75	108.2 (4.2)	101.6 (1.9)	65	106.7 (6.3)	102.2 (5.6)	62	95.9 (3.3)	103.9 (1.2)	42
178	Fluquinconazole	101.5 (2.6)	99.7 (1.1)	73	109.6 (4.3)	102.2 (1.8)	59	106.7 (3.6)	103.2 (3.1)	58	91.6 (2.6)	97.6 (4.1)	13
179	Flurochloridone	97.6 (11.8)	102.4 (3.7)	81	110.0 (15.3)	97.6 (4.5)	81	99.9 (7.4)	99.1 (4.0)	56	101.8 (11.4)	97.7 (3.1)	46
180	Flurtamone	106.8 (5.4)	97.6 (4.8)	189	106.9 (5.5)	100.9 (2.2)	206	104.8 (3.7)	103.5 (3.0)	180	92.0 (4.0)	93.7 (2.1)	72
181	Flusilazole	104.2 (6.1)	102.7 (2.4)	124	106.7 (3.5)	101.9 (3.6)	125	105.4 (7.1)	104.2 (4.7)	119	96.9 (2.9)	102.9 (2.0)	87
182	Fluthiacet-methyl	61.3 (11.2)	74.2 (1.7)	>500	113.0 (5.8)	122.5 (7.4)	355	89.7 (8.1)	79.9 (7.8)	>500	49.3 (9.7)	43.1 (10.1)	285
183	Flutianil	98.5 (3.3)	103.1 (1.2)	83	112.9 (4.8)	104.8 (2.8)	69	107.1 (3.5)	102.4 (3.0)	75	92.9 (2.8)	98.3 (2.4)	26
184	Flutolanil	105.7 (4.4)	103.1 (2.0)	-23	109.0 (5.1)	101.4 (2.9)	67	109.2 (1.6)	117.5 (3.0)	52	94.0 (3.8)	100.7 (1.9)	35
185	Flutriafol	91.3 (4.8)	105.0 (2.3)	-5	104.0 (4.3)	99.3 (3.5)	59	117.0 (5.9)	103.0 (4.6)	16	97.2 (4.2)	102.2 (1.8)	31
186	Fluvalinate	83.6 (3.3)	88.5 (2.0)	386	108.1 (3.6)	102.6 (3.0)	497	96.7 (2.4)	85.9 (2.4)	413	81.2 (2.3)	75.8 (6.9)	99
187	Folpet	N.D	32.7 (6.9)	377	121.7 (7.9)	118.2 (10.3)	480	47.1 (80.6)	8.4 (47.9)	265	47.3 (26.7)	45.4 (16.0)	369
188	Fonofos	101.8 (6.2)	101.4 (2.9)	72	106.9 (3.5)	101.2 (2.6)	66	107.8 (2.1)	101.9 (2.2)	68	92.0 (3.5)	102.3 (3.4)	30
189	Formothion	81.2 (7.7)	84.0 (2.8)	>500	111.6 (9.9)	107.9 (6.0)	336	91.4 (5.1)	86.4 (1.9)	439	86.2 (7.5)	91.5 (7.5)	191
190	Fosthiazate	55.7 (7.8)	77.0 (7.4)	282	112.5 (5.4)	103.5 (2.5)	420	83.5 (8.2)	75.9 (8.5)	248	103.1 (10.4)	79.4 (2.8)	290
191	Furathiocarb	98.4 (11.1)	99.2 (2.9)	412	108.0 (3.2)	103.5 (1.8)	413	104.8 (3.4)	66.1 (9.6)	395	101.2 (3.3)	92.8 (1.6)	238
192	Halfenprox	100.1 (5.3)	88.4 (1.6)	219	106.2 (3.6)	99.4 (3.3)	162	95.3 (3.6)	92.5 (2.6)	177	82.9 (3.8)	84.8 (1.2)	59
193	Heptachlor	106.4 (5.1)	95.8 (3.9)	48	110.9 (3.2)	96.6 (3.3)	40	96.2 (4.3)	87.6 (4.3)	9	94.1 (3.7)	94.8 (4.0)	23
194	Heptachlor epoxide	87.8 (7.0)	93.3 (3.1)	39	117.8 (7.8)	103.3 (3.7)	25	102.0 (5.7)	101.6 (3.3)	30	92.3 (6.1)	102.0 (1.1)	6
195	Heptenophos	101.9 (2.9)	94.9 (3.9)	155	108.4 (4.1)	100.8 (1.9)	180	103.2 (2.5)	92.3 (6.6)	143	83.5 (1.7)	97.8 (4.7)	95
196	Hexachlorobenzene	90.4 (8.4)	78.9 (2.7)	52	107.9 (4.1)	95.7 (4.2)	41	92.2 (5.8)	90.6 (4.7)	48	90.6 (4.7)	104.0 (5.9)	9
197	Hexaconazole	125.5 (14.0)	148.9 (9.2)	7	107.4 (9.0)	100.1 (3.1)	113	113.3 (10.8)	101.0 (6.1)	103	94.7 (3.6)	102.5 (2.6)	80
198	Hexazinone	102.7 (3.2)	98.8 (2.0)	109	101.5 (3.4)	98.1 (2.2)	115	107.3 (4.9)	102.0 (2.4)	99	98.6 (9.1)	97.1 (2.3)	64
199	Hexythiazox	N.D	29.2 (53.9)	>500	110.3 (6.3)	100.2 (8.2)	>500	105.6 (6.0)	98.0 (3.9)	>500	90.4 (5.1)	71.4 (32.8)	>500
200	Imazalil	N.D	99.6 (16.8)	-	N.D	N.D	-	N.D	N.D	-	78.4 (32.4)	117.6 (64.5)	-
201	Imibenconazole	100.5 (1.9)	99.6 (1.3)	>500	107.8 (3.3)	99.2 (2.9)	>500	97.9 (5.5)	96.2 (2.8)	>500	79.6 (7.3)	72.7 (8.9)	292
202	Indanofan	98.3 (5.6)	101.7 (2.6)	117	101.6 (8.1)	93.7 (3.0)	90	102.6 (11.6)	100.1 (4.3)	65	88.6 (10.2)	89.6 (2.3)	55
203	Indoxacarb	90.2 (5.3)	93.3 (3.2)	380	109.1 (6.2)	101.4 (4.7)	419	102.7 (2.6)	97.7 (2.5)	327	85.5 (8.4)	88.4 (4.0)	166
204	Ipconazole	100.8 (4.7)	97.7 (3.7)	93	103.6 (4.8)	96.2 (1.3)	95	105.3 (4.1)	99.3 (4.1)	82	94.1 (4.4)	97.1 (4.5)	54
205	Ipfencarbazone	84.5 (3.8)	87.9 (3.2)	209	112.0 (4.1)	106.3 (2.1)	236	100.5 (4.8)	96.2 (2.8)	203	91.2 (4.7)	89.6 (3.0)	124
206	Iprobenfos	102.2 (2.1)	100.8 (1.6)	114	108.0 (4.5)	100.4 (1.4)	101	105.3 (4.3)	94.5 (2.4)	93	91.4 (2.8)	98.5 (2.5)	62
207	Iprodione	81.2 (11.4)	85.4 (4.7)	>500	121.1 (5.6)	109.9 (3.0)	>500	84.4 (10.8)	94.0 (3.8)	>500	83.9 (32.2)	81.8 (10.2)	>500
208	Iprovalicarb	106.5 (11.0)	101.8 (2.9)	96	107.4 (7.4)	101.9 (2.0)	92	106.4 (7.7)	100.3 (5.9)	84	93.4 (3.2)	99.2 (2.3)	60
209	Isazofos	96.7 (5.2)	101.8 (2.9)	67	110.3 (4.5)	101.9 (2.5)	54	103.8 (10.1)	102.1 (4.2)	58	89.5 (3.0)	98.3 (2.7)	9
210	Isofenphos	102.5 (1.6)	104.0 (1.0)	57	109.2 (3.0)	102.7 (2.8)	50	110.2 (5.3)	106.2 (4.0)	52	95.7 (1.6)	104.0 (2.3)	28

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
211	Isofenphos-methyl	100.5 (3.0)	101.6 (2.2)	61	109.7 (4.3)	101.9 (2.6)	51	108.9 (2.9)	104.2 (3.3)	52	94.3 (2.2)	104.0 (1.2)	33
212	Isoprocarb	96.4 (5.0)	91.1 (2.4)	208	114.9 (5.0)	101.8 (2.1)	291	99.8 (2.3)	103.6 (3.3)	233	99.1 (3.1)	102.5 (10.2)	121
213	Isopropalin	101.9 (3.9)	95.7 (1.1)	80	105.9 (4.6)	99.0 (3.5)	62	101.4 (4.0)	99.3 (2.6)	70	86.7 (3.7)	92.3 (1.4)	27
214	Isoprothiolane	145.8 (19.2)	174.9 (7.9)	-34	109.5 (3.0)	102.1 (3.1)	54	110.8 (5.3)	103.8 (3.7)	41	96.2 (4.1)	105.3 (2.9)	32
215	Isoxadifen-ethyl	103.3 (4.5)	101.7 (2.4)	81	106.2 (5.8)	101.0 (2.2)	66	105.5 (2.7)	99.3 (3.4)	65	89.8 (4.1)	95.2 (2.0)	28
216	Isoxathion	118.8 (3.0)	103.6 (2.1)	176	105.0 (8.8)	92.4 (5.0)	130	112.6 (9.2)	86.0 (5.4)	60	81.3 (8.4)	71.4 (2.7)	149
217	Kresoxim-methyl	102.0 (4.7)	101.1 (2.5)	45	106.1 (4.6)	101.8 (3.0)	46	111.4 (3.8)	104.4 (4.0)	34	98.4 (2.1)	103.2 (3.1)	24
218	Lactofen	98.9 (3.8)	91.3 (1.6)	286	105.1 (4.8)	95.4 (2.4)	206	95.6 (5.3)	91.9 (4.0)	232	91.8 (9.5)	73.0 (6.4)	56
219	Leptophos	91.6 (2.2)	89.0 (1.5)	166	106.1 (3.1)	100.7 (1.9)	141	99.5 (2.7)	94.8 (2.4)	134	91.4 (2.9)	86.7 (2.0)	79
220	Malathion	96.4 (1.4)	98.7 (1.5)	141	108.1 (3.0)	98.9 (6.7)	139	105.8 (3.8)	97.9 (3.8)	125	89.1 (5.8)	97.7 (1.8)	86
221	Mecarbam	99.4 (10.2)	100.6 (5.0)	121	109.6 (4.8)	98.0 (5.2)	102	110.7 (7.1)	102.7 (3.5)	100	91.9 (7.3)	96.9 (2.3)	60
222	Mefenacet	103.9 (5.0)	98.4 (2.0)	365	101.8 (3.5)	98.9 (1.5)	366	102.2 (2.7)	102.1 (2.5)	324	94.2 (2.2)	88.2 (1.0)	202
223	Mefenpyr-diethyl	102.8 (1.9)	102.3 (1.2)	69	109.2 (4.7)	102.9 (2.4)	59	108.1 (2.7)	103.0 (3.3)	58	92.8 (2.2)	99.1 (1.9)	31
224	Mepanipyrim	N.D	106.1 (8.3)	-4	107.3 (3.7)	98.6 (5.5)	100	113.8 (19.7)	104.4 (3.0)	-1	92.8 (3.1)	98.7 (1.9)	52
225	Mepronil	104.3 (4.2)	102.2 (1.4)	137	107.1 (4.9)	101.3 (2.4)	128	106.4 (4.6)	104.0 (2.8)	121	95.1 (3.0)	102.6 (0.5)	66
226	Metalaxyl	96.4 (8.7)	104.5 (1.8)	46	101.1 (4.6)	99.0 (2.2)	42	111.9 (5.7)	103.5 (3.8)	42	99.4 (3.4)	100.5 (2.6)	18
227	Metconazole	108.3 (19.3)	104.3 (6.7)	128	98.1 (13.4)	94.9 (9.0)	136	85.9 (9.7)	99.1 (11.5)	125	59.9 (40.9)	85.5 (9.1)	68
228	Methidathion	91.7 (2.7)	93.0 (1.6)	221	105.4 (3.3)	100.8 (3.0)	159	100.4 (3.0)	92.3 (2.3)	148	95.9 (2.4)	88.9 (2.1)	119
229	Methoprotryne	102.6 (5.0)	101.4 (1.9)	67	103.5 (6.0)	100.4 (2.6)	67	107.4 (4.6)	99.4 (4.1)	65	97.3 (2.9)	100.7 (2.2)	38
230	Methoxychlor	126.9 (4.5)	117.8 (2.0)	20	120.0 (2.4)	106.6 (2.7)	57	123.1 (7.4)	80.0 (3.2)	-13	90.9 (3.6)	86.6 (1.6)	102
231	Metolachlor	100.0 (1.8)	101.8 (1.3)	52	107.6 (2.3)	102.8 (2.6)	45	106.0 (4.1)	103.0 (3.2)	45	94.5 (3.1)	103.7 (0.9)	23
232	Metrafenone	108.5 (6.5)	102.7 (3.5)	68	108.6 (4.1)	102.7 (3.9)	55	105.3 (3.6)	103.9 (4.0)	60	97.9 (4.3)	99.2 (1.0)	23
233	Metribuzin	107.2 (4.0)	102.4 (2.8)	77	98.4 (9.5)	93.6 (2.4)	55	108.2 (6.3)	100.8 (6.0)	48	95.4 (2.8)	99.2 (1.0)	34
234	Mevinphos	80.1 (5.4)	87.1 (2.9)	152	107.4 (2.7)	97.2 (2.6)	201	97.0 (3.9)	80.0 (4.7)	147	91.0 (1.5)	98.1 (5.1)	84
235	Mirex	82.9 (3.3)	77.8 (1.4)	46	105.0 (3.3)	98.3 (3.3)	45	80.5 (3.4)	87.6 (2.0)	18	93.7 (2.7)	97.4 (1.4)	28
236	Molinate	105.7 (6.6)	98.6 (3.7)	46	111.0 (3.9)	98.4 (3.0)	40	108.8 (4.6)	103.5 (3.8)	42	92.6 (1.7)	109.3 (6.1)	3
237	Myclobutanil	105.5 (2.4)	103.0 (0.7)	>500	107.4 (3.0)	100.9 (2.5)	>500	108.3 (2.2)	102.8 (3.3)	>500	96.0 (4.2)	100.9 (2.1)	>500
238	Napropamide	103.5 (7.3)	106.6 (3.7)	-31	108.9 (5.0)	100.6 (3.4)	45	109.3 (6.4)	118.2 (3.9)	22	92.8 (2.6)	102.8 (2.2)	21
239	Nitrapyrin	165.4 (43.1)	141.3 (34.4)	17	107.1 (11.0)	103.6 (7.7)	51	123.2 (5.9)	72.3 (13.4)	4	89.4 (4.5)	88.7 (10.8)	52
240	Nitrothal-isopropyl	103.5 (4.6)	96.4 (1.9)	117	106.7 (3.4)	98.3 (3.2)	94	103.4 (2.0)	98.4 (3.1)	106	93.1 (5.4)	87.7 (1.7)	42
241	Nonachlor-cis	85.6 (8.7)	91.7 (3.0)	31	107.1 (5.8)	100.8 (3.2)	34	99.4 (5.6)	96.1 (5.0)	24	96.9 (5.9)	97.1 (1.8)	11
242	Nonachlor-trans	96.3 (8.4)	88.2 (4.7)	-28	108.4 (5.1)	100.7 (7.3)	26	109.0 (5.6)	100.5 (3.0)	-10	94.8 (3.1)	97.7 (2.1)	8
243	Norflurazon	106.6 (6.3)	101.4 (0.9)	>500	103.7 (7.9)	100.6 (2.9)	>500	98.4 (8.7)	103.7 (3.6)	466	97.0 (4.3)	93.2 (3.1)	249
244	Nuarimol	102.3 (2.2)	100.4 (1.3)	60	105.6 (4.1)	99.6 (2.5)	60	110.8 (3.4)	100.5 (3.4)	52	95.3 (2.2)	100.1 (2.4)	30
245	Ofurace	88.9 (4.8)	91.0 (1.7)	171	110.1 (4.7)	103.1 (2.9)	205	98.8 (4.2)	97.6 (3.1)	163	97.4 (8.0)	87.2 (3.9)	94
246	Omethoate	51.4 (13.5)	65.9 (3.5)	>500	94.6 (5.3)	96.2 (8.0)	>500	48.9 (27)	43.8 (26.5)	>500	86.2 (16.3)	41.0 (5.3)	>500

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
247	Oryzalin	94.2 (11.3)	98.3 (4.7)	143	104.4 (7.8)	98.5 (3.3)	122	102.0 (7.8)	99.2 (3.2)	124	93.2 (5.0)	89.1 (3.1)	53
248	Oxadiazon	104.5 (2.0)	102.4 (1.7)	30	107.0 (1.0)	102.6 (4.2)	36	106.8 (7.1)	104.1 (3.3)	31	99.6 (2.5)	104.7 (1.4)	21
249	Oxadixyl	96.6 (4.8)	98.5 (1.0)	62	107.1 (3.4)	100.8 (1.6)	66	105.3 (2.7)	102.7 (3.3)	50	97.4 (6.5)	97.6 (2.0)	31
250	Oxyfluorfen	100.8 (11.6)	99.0 (5.4)	147	108.3 (11.9)	97.7 (2.7)	132	96.9 (8.5)	99.6 (4.3)	137	84.0 (6.3)	81.7 (5.8)	61
251	Paclobutrazol	100.4 (4.2)	98.7 (1.1)	67	107.1 (2.5)	100.6 (3.0)	61	110.2 (6.3)	103.1 (4.5)	59	91.5 (3.8)	102.6 (1.1)	33
252	Parathion	97.5 (5.4)	97.7 (2.4)	131	105.6 (2.6)	97.1 (1.5)	115	101.0 (4.2)	100.3 (4.1)	117	88.6 (7.6)	88.1 (2.0)	55
253	Parathion-methyl	105.4 (5.1)	97.8 (3.3)	201	104.6 (7.9)	99.4 (2.4)	161	97.7 (6.2)	95.6 (2.5)	158	87.5 (9.6)	82.8 (1.8)	77
254	Pebulate	100.2 (11.8)	98.2 (3.6)	39	111.4 (4.5)	98.6 (3.7)	29	113.1 (4.0)	99.0 (5.5)	34	95.8 (3.3)	108.0 (7.6)	1
255	Penconazole	100.1 (2.3)	100.2 (1.4)	54	107.2 (3.4)	100.4 (2.3)	45	105.0 (3.9)	103.0 (2.9)	46	94.1 (3.5)	103.1 (1.4)	22
256	Pencycuron	115.1 (4.5)	101.6 (2.1)	326	102.6 (5.5)	100.6 (6.3)	251	107.6 (10.3)	111.5 (8.0)	185	96.9 (3.3)	107.1 (3.0)	145
257	Pendimethalin	105.3 (6.8)	94.7 (1.7)	97	105.4 (7.8)	96.8 (3.1)	77	97.0 (6.7)	99.2 (2.3)	86	86.9 (7.8)	91.3 (3.1)	19
258	Pentachloroaniline	101.3 (4.7)	91.5 (2.9)	70	111.7 (5.6)	100.3 (2.8)	60	104.7 (7.3)	100.3 (2.3)	65	97.0 (6.1)	105.3 (1.8)	29
259	Pentachlorothioanisole	91.8 (4.4)	82.2 (3.7)	30	108.0 (3.9)	93.5 (10.6)	44	95.7 (9.0)	94.4 (1.8)	27	98.1 (3.0)	90.4 (1.9)	27
260	Penthiopyrad	104.4 (3.7)	102.9 (1.4)	74	108.9 (4.4)	103.7 (2.0)	61	107.3 (4.6)	105.1 (4.1)	64	94.2 (1.5)	100.4 (2.0)	31
261	Permethrin	90.3 (14.1)	90.1 (1.6)	88	107.3 (3.4)	101.1 (4.0)	88	117.4 (5.9)	96.1 (3.2)	83	89.6 (2.8)	95.5 (2.6)	37
262	Phenothrin	643.1 (21.7)	187.6 (16.9)	193	33.9 (148.3)	148.6 (46.4)	46	433.6 (56.3)	104.4 (3.4)	64	91.0 (3.6)	100.9 (2.0)	66
263	Phenthoate	101.0 (3.6)	99.5 (1.8)	91	107.4 (4.7)	102.1 (3.0)	72	102.4 (3.6)	100.4 (3.3)	72	86.7 (2.8)	98.8 (2.1)	39
264	Phorate	107.6 (5.8)	99.0 (2.7)	82	107.2 (7.0)	100.5 (2.5)	65	107.6 (3.5)	99.1 (2.9)	76	89.2 (3.3)	102.6 (3.6)	36
265	Phosalone	92.9 (5.3)	94.3 (1.9)	254	107.4 (3.3)	101.6 (1.8)	215	104.2 (2.5)	94.6 (2.5)	188	94.7 (2.6)	83.5 (2.8)	102
266	Phosmet	77.8 (4.3)	83.5 (3.1)	>500	106.1 (4.4)	107.9 (8.9)	>500	87.6 (7.9)	83.3 (6.6)	>500	90.7 (8.9)	52.1 (3.6)	345
267	Phosphamidon	66.1 (14.7)	78.9 (4.7)	376	106.8 (6.4)	101.8 (4.6)	344	80.8 (8.3)	71.2 (11.8)	284	98.6 (10.0)	84.5 (3.0)	278
268	Phthalide	99.6 (1.4)	98.4 (1.9)	122	97.6 (4.5)	95.0 (3.6)	112	101.1 (4.8)	102.1 (3.5)	102	98.2 (3.4)	99.1 (2.7)	67
269	Picolinafen	99.7 (2.5)	100.9 (1.0)	79	109.4 (2.8)	103.8 (2.8)	71	103.5 (4.2)	104.4 (3.2)	71	93.5 (3.1)	98.0 (1.6)	36
270	Picoxystrobin	97.3 (3.9)	103.6 (2.9)	50	111.1 (4.2)	102.8 (3.2)	41	110.1 (4.2)	103.5 (3.8)	42	94.8 (5.3)	104.7 (2.0)	11
271	Piperonyl butoxide	101.8 (2.0)	101.7 (0.9)	103	107.6 (3.8)	100.8 (2.4)	92	106.0 (4.1)	102.7 (2.6)	86	94.7 (1.6)	101.6 (2.0)	54
272	Piperophos	102.3 (3.1)	103.3 (1.1)	128	107.9 (4.5)	101.0 (2.0)	112	102.9 (5.5)	102.4 (2.9)	117	90.0 (3.6)	93.0 (1.5)	56
273	Pirimicarb	102.0 (5.1)	103.7 (1.6)	70	103.6 (4.7)	97.0 (2.5)	63	106.5 (4.9)	95.7 (1.1)	63	94.9 (2.9)	102.2 (2.1)	30
274	Pirimiphos ethyl	99.0 (5.9)	100.6 (2.9)	55	109.0 (2.7)	101.2 (2.7)	44	103.3 (4.1)	101.1 (2.7)	45	99.5 (6.1)	103.3 (3.5)	20
275	Pirimiphos methyl	99.5 (5.7)	99.8 (3.3)	61	108.7 (5.6)	101.9 (2.8)	52	104.8 (4.5)	99.9 (2.9)	48	92.8 (2.4)	100.5 (1.6)	28
276	Pretilachlor	111.0 (3.5)	108.1 (2.3)	18	108.9 (4.7)	101.6 (3.4)	54	103.5 (5.5)	101.6 (2.8)	45	94.2 (3.3)	99.3 (2.1)	26
277	Prochloraz	103.9 (9.3)	93.0 (4.2)	327	102.9 (4.3)	90.3 (3.8)	289	100.3 (4.3)	94.7 (1.8)	215	88.3 (11.2)	90.7 (4.1)	163
278	Procymidone	100.7 (3.9)	103.5 (1.3)	41	107.0 (4.6)	101.7 (3.1)	37	109.5 (6.2)	102.9 (3.9)	35	99.9 (2.8)	104.6 (1.3)	14
279	Profenofos	82.1 (5.9)	87.5 (2.6)	163	112.6 (4.7)	101.2 (3.8)	246	88.7 (7.7)	90.7 (7.6)	176	69.4 (75.3)	89.8 (3.1)	161
280	Profluralin	102.0 (5.4)	96.8 (4.7)	73	115.4 (3.4)	98.3 (4.4)	60	104.7 (5.2)	102.9 (8.3)	59	88.1 (4.7)	89.7 (1.7)	4
281	Promecarb	92.6 (14.7)	96.5 (5.6)	408	109.3 (3.6)	102.6 (1.3)	>500	95.2 (8.1)	96.5 (1.9)	465	94.2 (4.3)	90.6 (6.8)	209
282	Prometon	102.8 (5.2)	100.4 (1.5)	127	102.7 (4.6)	99.5 (2.4)	117	105.9 (5.5)	102.4 (4.3)	109	95.8 (3.9)	102.8 (2.8)	68

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
283	Prometryn	108.2 (7.3)	107.2 (2.2)	47	107.2 (3.6)	101.3 (2.3)	41	115.6 (14.5)	105.9 (5.1)	35	100.5 (3.3)	105.9 (1.9)	16
284	Propachlor	100.6 (5.7)	97.0 (4.9)	87	107.5 (2.7)	100.9 (2.5)	95	106.9 (3.4)	99.4 (4.0)	88	95.5 (0.7)	101.7 (4.6)	41
285	Propanil	77.7 (25.1)	93.6 (8.6)	>500	102.6 (4.7)	99.2 (1.9)	>500	104.7 (8.5)	102.8 (2.6)	>500	96.4 (1.8)	98.7 (6.7)	>500
286	Propaquizafop	103.5 (3.7)	101.7 (0.8)	52	104.1 (4.2)	93.7 (2.4)	44	101.3 (3.2)	98.8 (1.5)	25	25.7 (14.7)	59.0 (6.7)	-42
287	Propargite	98.3 (14.5)	95.2 (3.1)	42	112.1 (4.9)	106.4 (2.1)	49	104.1 (5.5)	95.2 (2.7)	28	113.2 (36.7)	111.4 (3.1)	32
288	Propazine	91.1 (3.9)	100.6 (2.1)	87	104.8 (7.0)	100.9 (3.1)	75	105.6 (5.0)	103.1 (2.3)	76	96.6 (4.9)	102.7 (2.1)	47
289	Propetamphos	104.7 (8.3)	102.9 (2.4)	93	109.3 (4.5)	101.4 (3.6)	84	104.1 (5.6)	102.3 (2.5)	83	92.3 (2.9)	100.0 (1.5)	43
290	Propham	111.0 (6.7)	104.0 (2.9)	79	109.5 (2.9)	102.1 (4.1)	90	104.9 (2.8)	103.7 (4.7)	77	91.5 (3.7)	108.8 (6.6)	19
291	Propiconazole	98.7 (5.8)	101.9 (1.9)	51	107.7 (3.7)	100.1 (2.3)	62	107.9 (4.2)	101.9 (3.3)	51	94.0 (3.3)	98.7 (2.1)	32
292	Propisochlor	103.5 (4.1)	101.4 (1.7)	54	95.5 (6.4)	101.2 (4.0)	43	107.8 (2.2)	104.2 (3.2)	47	93.8 (6.7)	99.7 (2.1)	13
293	Propyzamide	104.1 (1.6)	99.6 (1.3)	92	105.0 (6.2)	97.9 (3.0)	83	111.5 (4.0)	104.2 (4.7)	77	95.2 (2.9)	99.2 (6.1)	41
294	Prosulfocarb	104.9 (4.0)	99.2 (2.4)	74	111.8 (3.9)	101.1 (4.4)	62	103.1 (4.5)	101.1 (2.9)	67	93.4 (2.1)	101.2 (2.3)	25
295	Prothiofos	104.0 (19.3)	151.8 (11.1)	-47	108.5 (2.4)	100.6 (3.8)	50	102.9 (4.4)	99.7 (3.8)	37	95.5 (3.5)	99.7 (1.4)	23
296	Pyracarbolid	106.2 (3.8)	100.6 (1.9)	231	102.7 (6.7)	99.2 (3.3)	209	106.3 (5.0)	101.7 (3.9)	199	98.3 (3.6)	97.1 (6.3)	134
297	Pyraclofos	75.9 (7.4)	82.4 (3.7)	>500	110.3 (3.5)	99.4 (2.5)	>500	85.8 (3.8)	76.3 (7.9)	>500	87.6 (7.7)	76.7 (3.7)	>500
298	Pyraclostrobin	73.9 (41.9)	85.5 (5.5)	>500	98.2 (10.2)	101.9 (4.5)	>500	85.3 (38.4)	92.7 (3.8)	>500	85.9 (7.6)	76.0 (6.0)	>500
299	Pyrazophos	97.6 (3.7)	98.6 (1.4)	187	107.3 (3.4)	101.3 (2.5)	148	103.4 (2.6)	99.6 (2.1)	154	89.3 (2.1)	90.0 (1.7)	83
300	Pyributicarb	102.6 (2.1)	99.4 (2.0)	92	107.0 (3.1)	102.1 (2.2)	77	104.4 (4.0)	103.4 (3.3)	78	91.7 (1.1)	97.5 (1.7)	35
301	Pyridaben	106.7 (7.8)	97.7 (2.6)	116	94.9 (6.0)	100.9 (4.6)	102	103.9 (4.1)	99.5 (3.0)	99	88.0 (1.4)	94.7 (1.6)	37
302	Pyridalyl	94.4 (3.2)	90.0 (1.4)	147	107.2 (5.0)	100.2 (4.5)	123	97.5 (4.7)	96.9 (2.7)	126	90.0 (2.1)	94.9 (2.5)	53
303	Pyridaphenthion	101.6 (3.8)	98.1 (2.2)	230	110.3 (4.1)	100.6 (1.8)	169	98.6 (4.0)	95.0 (2.5)	176	87.6 (5.0)	86.0 (2.0)	86
304	Pyrifenox	103.8 (2.2)	99.7 (1.7)	72	105.2 (3.6)	97.4 (2.4)	66	99.5 (4.3)	96.7 (4.7)	54	94.1 (3.6)	102.1 (2.4)	36
305	Pyrimethanil	99.6 (4.1)	95.3 (1.9)	102	103.9 (5.9)	96.9 (4.0)	89	105.2 (3.7)	99.6 (3.1)	88	95.1 (4.3)	108.7 (11.9)	24
306	Pyrimidifen	104.9 (2.9)	94.4 (3.1)	123	106.4 (3.6)	100.6 (2.2)	112	106.4 (4.0)	102.0 (3.2)	111	92.1 (2.8)	98.2 (2.4)	52
307	Pyriminobac-methyl (E)	104.9 (2.2)	103.3 (1.6)	69	108.8 (3.7)	101.4 (1.8)	57	104.0 (3.2)	104.3 (2.9)	53	94.4 (3.4)	99.3 (1.4)	31
308	Pyriminobac-methyl (Z)	100.4 (3.5)	103.1 (1.2)	62	106.3 (2.6)	101.3 (2.5)	54	106.4 (4.4)	103.7 (3.2)	52	94.1 (1.0)	102.6 (1.2)	26
309	Pyriproxyfen	94.1 (12.3)	97.9 (1.7)	141	108.2 (4.6)	100.6 (3.0)	135	104.7 (3.8)	101.2 (4.0)	129	91.2 (3.0)	102.2 (2.7)	73
310	Pyroquilon	100.5 (3.5)	99.3 (2.3)	140	97.6 (3.4)	96.6 (3.1)	142	107.2 (3.9)	96.0 (6.2)	137	98.0 (3.5)	101.6 (2.8)	67
311	Quinalphos	106.3 (3.9)	100.3 (1.6)	68	106.5 (3.5)	100.9 (2.7)	58	107.7 (4.9)	102.6 (2.4)	53	93.8 (4.3)	102.9 (1.8)	30
312	Quinoxyfen	95.4 (3.1)	95.6 (1.1)	62	106.0 (2.4)	100.5 (2.8)	57	102.9 (3.8)	99.9 (3.2)	53	97.1 (3.1)	100.1 (1.1)	28
313	Quintozene	102.9 (8.4)	90.8 (8.1)	97	112.8 (9.1)	103.3 (5.6)	91	97.2 (4.2)	97.5 (5.5)	96	102.9 (6.1)	91.2 (3.1)	32
314	Quizalofop-ethyl	101.6 (2.9)	102.8 (1.5)	290	108.8 (3.3)	101.7 (2.7)	264	104.1 (2.6)	103.1 (3.2)	268	73.5 (2.9)	88.6 (3.4)	144
315	Resmethrin	94.7 (5.3)	95.9 (2.2)	86	104.7 (4.5)	99.9 (3.0)	72	97.8 (2.7)	98.7 (1.9)	65	96.4 (3.1)	101.1 (1.4)	32
316	Secbumeton	108.4 (16.1)	104.8 (3.3)	76	103.5 (3.7)	95.5 (3.2)	63	112.1 (6.5)	94.6 (4.7)	51	98.2 (8.1)	104.1 (3.1)	24
317	Silafluofen	97.2 (3.8)	94.4 (1.4)	78	118.8 (7.7)	104.1 (5.0)	62	97.0 (3.8)	100.1 (3.3)	66	96.1 (1.3)	99.0 (3.1)	29
318	Simazine	98.3 (4.1)	99.8 (5.3)	154	103.3 (10.8)	99.1 (2.4)	146	112.0 (6.0)	104.4 (3.4)	135	91.5 (1.7)	101.3 (7.7)	74

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
319	Simeconazole	101.8 (8.6)	102.4 (1.6)	65	108.0 (3.0)	101.5 (2.9)	58	108.6 (7.1)	103.1 (6.3)	57	97.3 (6.0)	101.1 (2.3)	30
320	Simetryn	103.3 (4.5)	100.2 (3.8)	77	102.3 (5.3)	96.2 (2.5)	70	108.8 (7.5)	100.3 (3.6)	72	92.3 (3.5)	101.6 (2.2)	33
321	Spirodiclofen	68.2 (11.7)	89.5 (4.2)	109	115.4 (4.4)	110.2 (2.7)	112	93.0 (2.8)	85.1 (3.8)	103	96.7 (14.1)	86.7 (5.8)	31
322	Spiromesifen	90.2 (1.8)	95.6 (1.3)	88	110.9 (3.5)	106.2 (2.4)	74	100.2 (4.6)	93.2 (3.4)	81	95.1 (4.6)	94.8 (2.0)	35
323	Sulfotep	104.7 (2.6)	101.1 (2.7)	60	110.7 (3.7)	100.4 (3.2)	53	106.0 (5.8)	102.5 (3.8)	51	96.5 (4.8)	101.1 (4.1)	16
324	Sulprofos	96.8 (7.1)	94.9 (2.5)	81	108.3 (3.1)	100.2 (1.6)	64	100.8 (3.8)	100.9 (3.0)	64	96.2 (3.1)	96.3 (2.3)	28
325	Tebuconazole	98.7 (1.7)	103.0 (1.3)	63	104.5 (3.6)	100.1 (2.3)	67	106.2 (3.8)	102.8 (2.9)	64	94.4 (4.3)	101.1 (2.0)	35
326	Tebufenpyrad	101.7 (4.1)	102.5 (1.4)	67	106.8 (4.7)	102.8 (3.2)	56	107.0 (2.8)	103.6 (3.3)	59	95.7 (3.6)	101.3 (1.6)	24
327	Tebupirimfos	100.6 (9.1)	102.2 (3.2)	50	109.2 (4.9)	100.5 (1.5)	42	106.4 (5.3)	102.4 (3.8)	34	91.9 (5.3)	103.8 (5.1)	11
328	Tecnazene	107.5 (6.9)	95.8 (4.8)	75	111.5 (4.4)	99.2 (4.1)	72	108.4 (3.1)	100.7 (6.0)	69	95.6 (4.9)	99.0 (6.7)	14
329	Tefluthrin	102.2 (4.1)	99.4 (2.0)	44	109.2 (3.9)	100.9 (2.9)	37	107.3 (4.6)	101.9 (2.5)	34	93.6 (2.5)	103.4 (1.8)	16
330	Tepraloxydim	149.3 (14.3)	127.6 (4.0)	219	110.0 (4.2)	98.2 (6.1)	402	113.2 (3.6)	109.3 (10.2)	327	99.2 (15.5)	64.7 (12.0)	272
331	Terbacil	103.2 (5.9)	99.0 (1.6)	233	101.3 (12.6)	99.0 (1.5)	206	101.7 (5.1)	83.0 (5.7)	160	94.5 (15.7)	94.1 (3.1)	147
332	Terbufos	105.6 (3.9)	99.3 (1.8)	70	109.6 (4.5)	100.8 (3.5)	58	109.2 (1.3)	101.6 (4.2)	54	91.2 (1.9)	99.3 (3.3)	24
333	Terbumeton	103.6 (5.9)	101.9 (2.7)	80	108.4 (2.5)	99.1 (1.3)	67	104.4 (6.4)	105.0 (3.3)	68	94.5 (3.6)	102.2 (1.7)	29
334	Terbuthylazine	107.8 (6.6)	99.9 (3.2)	84	108.6 (2.6)	100.9 (3.0)	71	106.6 (4.9)	100.0 (1.9)	74	93.0 (3.8)	101.3 (2.1)	38
335	Terbutryn	93.0 (2.5)	99.7 (1.2)	55	108.7 (4.7)	101.3 (3.5)	45	113.3 (5.9)	116.2 (4.9)	51	76.9 (49.4)	101.4 (1.3)	22
336	Tetrachlorvinphos	58.0 (7.4)	74.6 (2.6)	277	110.7 (3.5)	102.6 (3.4)	352	81.8 (7.6)	75.2 (9.0)	259	97.0 (5.0)	82.2 (1.6)	247
337	Tetraconazole	104.5 (6.4)	104.1 (2.0)	57	109.1 (4.8)	101.2 (3.3)	47	104.2 (3.8)	103.6 (2.3)	51	99.4 (5.1)	99.8 (3.2)	27
338	Tetradifon	101.4 (6.3)	97.4 (2.9)	56	111.8 (4.6)	103.6 (5.0)	51	102.7 (2.7)	103.6 (4.2)	50	97.0 (2.7)	100.5 (4.8)	22
339	Thenylchlor	94.5 (12.4)	95.5 (1.9)	83	105.6 (4.8)	100.9 (2.4)	89	103.0 (3.4)	97.9 (1.4)	69	97.0 (2.8)	97.8 (1.2)	62
340	Thiazopyr	106.6 (8.4)	109.8 (2.7)	32	111.8 (5.5)	98.5 (5.2)	40	97.4 (3.9)	105.9 (4.7)	33	99.1 (5.7)	102.3 (3.3)	18
341	Thifluzamide	96.8 (6.4)	95.8 (3.2)	102	119.8 (4.7)	106.9 (3.5)	84	105.2 (5.5)	104.2 (5.3)	97	99.5 (5.3)	99.5 (1.1)	53
342	Thiobencarb	99.1 (6.4)	99.5 (1.9)	77	105.8 (3.2)	100.6 (2.0)	71	104.6 (6.0)	102.3 (3.3)	64	95.8 (1.9)	105.4 (2.0)	36
343	Thiometon	101.9 (10.4)	93.8 (8.8)	111	104.8 (7.2)	100.0 (2.6)	127	105.3 (4.6)	92.2 (5.5)	118	92.1 (6.9)	102.2 (2.5)	54
344	Tolclofos-methyl	105.1 (3.8)	99.1 (2.0)	65	108.0 (4.2)	100.7 (2.3)	54	104.5 (4.6)	102.9 (3.5)	52	93.8 (2.1)	101.8 (2.1)	25
345	Tolfenpyrad	98.5 (7.5)	103.4 (4.4)	-	104.3 (8.9)	103.4 (5.5)	-	101.3 (4.4)	107.2 (8.7)	-	92.3 (8.7)	94.0 (3.4)	-
346	Tolylfluanid	62.1 (7.5)	28.5 (2.1)	>500	122.6 (4.4)	94.0 (3.4)	>500	74.3 (8.5)	11.8 (10.4)	>500	108.9 (5.2)	65.8 (8.0)	406
347	Triadimefon	100.4 (7.1)	103.8 (4.3)	61	104.2 (6.8)	98.4 (2.8)	54	108.7 (4.6)	102.5 (4.2)	50	93.4 (4.6)	104.8 (4.4)	27
348	Triadimenol	99.3 (3.6)	99.2 (2.1)	58	109.4 (3.3)	99.8 (2.0)	54	110.7 (4.4)	102.7 (4.5)	44	73.9 (90.4)	101.5 (3.6)	26
349	Tri-allate	103.7 (5.1)	98.0 (2.5)	49	109.1 (3.1)	100.6 (3.2)	40	104.7 (4.3)	100.3 (3.7)	39	90.0 (5.1)	102.9 (3.1)	12
350	Triazophos	95.0 (4.0)	98.2 (1.6)	173	108.2 (4.0)	100.3 (2.3)	158	97.3 (2.8)	99.8 (2.3)	143	95.4 (3.2)	89.7 (1.8)	80
351	Tribufos	101.7 (6.2)	96.0 (1.5)	99	106.2 (5.4)	101.9 (2.6)	94	99.8 (5.1)	100.5 (3.3)	93	93.3 (2.6)	99.7 (1.6)	56
352	Tricyclazole	104.7 (4.6)	84.8 (3.9)	>500	88.7 (5.1)	82.2 (4.7)	>500	29.8 (13.8)	100.4 (2.7)	>500	93.8 (11.6)	409.6 (51.8)	>500
353	Trifloxystrobin	105.7 (2.2)	100.9 (1.4)	75	104.5 (3.3)	101.1 (1.5)	66	107.2 (6.1)	101.9 (3.5)	57	95.4 (1.9)	100.8 (1.6)	33
354	Triflumizole	107.9 (6.7)	102.0 (3.0)	68	106.3 (4.8)	97.9 (4.1)	59	103.4 (4.1)	102.2 (2.9)	56	93.0 (4.1)	98.8 (3.6)	32

No.	Compounds	Brown rice recovery, % (RSD, %)			Orange recovery, % (RSD, %)			Spinach recovery, % (RSD, %)			Potato recovery, % (RSD, %)		
		0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %	0.01 mg/kg	0.05 mg/kg	ME, %
355	Trifluralin	111.5 (3.5)	100.7 (3.6)	68	108.3 (4.8)	99.4 (3.9)	55	106.6 (4.3)	100.6 (3.8)	57	87.3 (3.6)	94.5 (4.4)	3
356	Triticonazole	104.1 (2.1)	99.7 (2.0)	101	107.8 (3.0)	99.2 (1.4)	96	103.3 (3.2)	100.0 (2.8)	93	90.8 (5.2)	95.9 (5.2)	37
357	Uniconazole	95.7 (5.3)	84.6 (9.2)	>500	108.5 (4.5)	102 (2.8)	>500	97.8 (11.8)	103.0 (3.3)	>500	96.0 (3.6)	99.2 (2.1)	>500
358	Vernolate	109.9 (7.7)	98.8 (3.6)	38	113.0 (9.5)	101.8 (3.1)	23	112.1 (4.0)	99.6 (7.7)	31	94.0 (4.5)	107.5 (8.4)	2
359	Vinclozolin	103.5 (5.2)	99.3 (5.4)	72	115.9 (5.5)	105.2 (5.0)	60	112.4 (7.9)	104.6 (8.5)	64	99.3 (12.0)	102.3 (4.7)	42

Table S4. Acquisition and chromatographic parameters for LC–MS/MS.

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
1	2,4-D	4.70	221	$[M-H]^-$	219.2 < 161.0 (12)	219.2 < 125.0 (24)
2	Abamectin B1a	9.42	873	$[M+Na]^+$	895.1 < 751.1 (-43)	895.1 < 449.1 (-48)
3	Acephate	2.85	183	$[M+H]^+$	183.6 < 143.0 (-10)	183.6 < 49.1 (-22)
4	Acetamiprid	3.28	222	$[M+H]^+$	222.6 < 126.0 (-20)	222.6 < 56.1 (-15)
5	Acibenzolar-S-methyl	5.48	210	$[M+H]^+$	210.8 < 136.0 (-29)	210.8 < 91.1 (-21)
6	Alachlor	8.05	269	$[M+H]^+$	269.7 < 238.0 (-11)	269.7 < 162.1 (-20)
7	Aldicarb	3.81	190	$[M+Na]^+$	212.9 < 89.1 (-16)	212.9 < 116.0 (-13)
8	Allidochlor	3.79	173	$[M+H]^+$	173.9 < 98.1 (-14)	173.9 < 41.1 (-24)
9	Ametoctradin	7.28	275	$[M+H]^+$	275.7 < 149.1 (-37)	275.7 < 176.1 (-36)
10	Ametryn	5.01	227	$[M+H]^+$	227.6 < 186.0 (-19)	227.6 < 68.0 (-38)
11	Amisulbrom	7.78	465	$[M+H]^+$	465.7 < 226.9 (-21)	465.7 < 148.0 (-51)
12	Amitraz	8.78	293	$[M+H]^+$	293.6 < 163.1 (-17)	293.6 < 122.1 (-28)
13	Anilofos	6.61	367	$[M+H]^+$	367.5 < 125.0 (-31)	367.5 < 198.9 (-15)
14	Asulam	2.92	230	$[M+H]^+$	231.0 < 155.9 (-11)	231.0 < 92.1 (-24)
15	Atrazine	4.7	215	$[M+H]^+$	215.7 < 174.0 (-18)	215.7 < 104.0 (-28)
16	Azaconazole	4.76	299	$[M+H]^+$	299.5 < 158.9 (-27)	299.5 < 230.9 (-17)
17	Azamethiphos	3.84	324	$[M+H]^+$	324.5 < 183.0 (-16)	324.5 < 112.1 (-36)
18	Azimsulfuron	4.56	424	$[M+H]^+$	424.6 < 182.0 (-19)	424.6 < 139.0 (-41)
19	Azinphos-methyl	4.99	317	$[M+H]^+$	317.8 < 77.0 (-39)	317.8 < 260.9 (-9)
20	Azoxystrobin	5.07	403	$[M+H]^+$	403.6 < 372.0 (-17)	403.6 < 344.0 (-25)
21	Bendiocarb	3.98	223	$[M+H]^+$	223.6 < 109.0 (-18)	223.6 < 167.1 (-10)
22	Bensulfuron-methyl	4.9	410	$[M+H]^+$	410.6 < 149.0 (-20)	410.6 < 182.0 (-20)
23	Bensulide	6.33	397	$[M+H]^+$	397.8 < 158.0 (-24)	397.8 < 313.9 (-11)
24	Bentazone	3.76	240	$[M-H]^-$	238.9 < 132.0 (24)	238.9 < 197.1 (19)
25	Benthiavalicarb-isopropyl	5.63	381	$[M+H]^+$	381.6 < 180.0 (-33)	381.6 < 116.1 (-21)
26	Benzobicyclon	5.49	447	$[M+H]^+$	446.5 < 257.0 (-24)	446.5 < 229.0 (-36)
27	Benzoximate	7.33	363	$[M+H]^+$	363.9 < 198.9 (-12)	363.9 < 105.0 (-26)
28	Bifenazate	5.78	300	$[M+H]^+$	300.6 < 198.0 (-10)	300.6 < 170.1 (-20)
29	Bromacil	4.07	260	$[M+H]^+$	260.8 < 204.9 (-14)	260.8 < 187.9 (-28)
30	Bromobutide	6.11	311	$[M+H]^+$	311.8 < 194.0 (-13)	311.8 < 119.1 (-20)
31	Bromoxynil	4.68	275	$[M+H]^+$	273.7 < 78.9 (-27)	273.7 < 167.0 (-30)
32	Bupirimate	6.14	316	$[M+H]^+$	316.6 < 166.1 (-24)	316.6 < 210.1 (-24)
33	Buprofezin	7.9	305	$[M+H]^+$	305.7 < 57.1 (-24)	305.7 < 116.0 (-16)
34	Butachlor	8.04	311	$[M+H]^+$	312.1 < 238.1 (-13)	312.1 < 57.2 (-22)
35	Butafenacil	5.86	474	$[M+NH_4]^+$	491.6 < 331.0 (-25)	491.6 < 180.0 (-45)
36	Butocarboxim	3.63	190	$[M+Na]^+$	212.9 < 75.0 (-15)	212.9 < 156.1 (-11)
37	Cadusafos	7.27	270	$[M+H]^+$	270.6 < 158.9 (-17)	270.6 < 130.9 (-22)
38	Carbaryl	4.18	201	$[M+H]^+$	201.8 < 145.1 (-11)	201.8 < 127.1 (-26)
39	Carbendazim	3.16	191	$[M+H]^+$	191.6 < 159.8 (-24)	191.6 < 132.1 (-29)
40	Carbofuran	4.01	221	$[M+H]^+$	221.6 < 123.0 (-21)	221.6 < 165.1 (-11)
41	Carbophenothion	8.44	342	$[M+H]^+$	342.8 < 157.0 (-13)	342.8 < 45.0 (-37)
42	Carboxin	4.2	235	$[M+H]^+$	235.6 < 143.0 (-15)	235.6 < 87.0 (-25)
43	Carfentrazone-ethyl	6.49	411	$[M+H]^+$	411.8 < 345.9 (-24)	411.8 < 365.9 (-18)
44	Carpropamid	6.71	333	$[M+H]^+$	333.6 < 139.0 (-21)	333.6 < 103.1 (-42)
45	Chinomethionat	7.72	234	$[M+H]^+$	235.0 < 207.0 (-15)	235.0 < 163.1 (-28)
46	Chlorantraniliprole	4.86	483	$[M+H]^+$	483.5 < 452.8 (-18)	483.5 < 285.9 (-16)
47	Chlorfenvinphos	6.75	358	$[M+H]^+$	358.5 < 99.0 (-30)	358.5 < 155.0 (-14)

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
48	Chlorfluazuron	8.76	539	$[M+H]^+$	539.8 < 382.8 (-23)	539.8 < 158.0 (-20)
49	Chloridazon	3.37	221	$[M+H]^+$	221.5 < 104.1 (-22)	221.5 < 77.0 (-35)
50	Chlorimuron-ethyl	5.72	414	$[M+H]^+$	414.5 < 186.0 (-19)	414.5 < 121.0 (-41)
51	Chlorotoluron	4.48	212	$[M+H]^+$	212.7 < 72.1 (-22)	212.7 < 46.2 (-16)
52	Chlorpyrifos	8.24	351	$[M+H]^+$	351.9 < 199.8 (-19)	351.9 < 97.0 (-31)
53	Chlorpyrifos-methyl	7.25	321	$[M+H]^+$	321.7 < 125.0 (-20)	321.7 < 289.8 (-15)
54	Chlorsulfuron	4.26	357	$[M+H]^+$	358.0 < 141.0 (-20)	358.0 < 167.0 (-19)
55	Chromafenozide	5.91	394	$[M+H]^+$	394.8 < 175.1 (-19)	394.8 < 147.0 (-44)
56	Clethodim	7.56	359	$[M+H]^+$	359.6 < 164.0 (-20)	359.6 < 166.1 (-26)
57	Clofentezine	7.07	302	$[M+H]^+$	303.0 < 138.0 (-15)	303.0 < 102.1 (-35)
58	Clomazone	5.06	239	$[M+H]^+$	239.6 < 125.0 (-20)	239.6 < 89.1 (-49)
59	Clomeprop	7.82	323	$[M+H]^+$	324.0 < 120.1 (-21)	324.0 < 203.0 (-17)
60	Clothianidin	3.21	249	$[M+H]^+$	250.0 < 169.0 (-13)	250.0 < 132.0 (-18)
61	Cyanazine	3.81	240	$[M+H]^+$	240.8 < 214.1 (-17)	240.8 < 104.0 (-30)
62	Cyazofamid	6.06	324	$[M+H]^+$	325.0 < 108.0 (-13)	325.0 < 261.0 (-10)
63	Cycloate	7.31	215	$[M+H]^+$	216.1 < 83.2 (-16)	216.1 < 55.0 (-30)
64	Cycloprothrin	8.64	481	$[M+NH_4]^+$	499.0 < 181.1 (-33)	499.0 < 256.9 (-16)
65	Cyclosulfamuron	5.8	421	$[M+H]^+$	421.6 < 261.0 (-19)	421.6 < 218.0 (-26)
66	Cyflufenamid	6.99	412	$[M+H]^+$	412.6 < 295.0 (-16)	412.6 < 241.0 (-24)
67	Cymoxanil	3.45	198	$[M+H]^+$	198.9 < 128.1 (-10)	198.9 < 111.1 (-18)
68	Cyproconazole	5.83	291	$[M+H]^+$	291.8 < 70.0 (-21)	291.8 < 125.0 (-31)
69	Cyprodidil	6.72	225	$[M+H]^+$	225.6 < 93.0 (-34)	225.6 < 108.0 (-25)
70	Cyromazine	1.26	166	$[M+H]^+$	166.8 < 85.1 (-19)	166.8 < 68.1 (-32)
71	Daimuron	5.66	268	$[M+H]^+$	269.0 < 151.0 (-20)	269.0 < 91.0 (-50)
72	Deltamethrin	8.9	505	$[M+NH_4]^+$	522.8 < 280.8 (-17)	522.8 < 505.9 (-11)
73	Demeton-S-Methyl	4.07	230	$[M+H]^+$	231.0 < 89.1 (-12)	231.0 < 61.1 (-32)
74	Diafenthiuron	8.88	384	$[M+H]^+$	384.6 < 329.0 (-19)	384.6 < 278.0 (-32)
75	Di-allate	7.49	269	$[M+H]^+$	270.0 < 86.1 (-17)	270.0 < 43.1 (-24)
76	Diazinon	6.81	304	$[M+H]^+$	305.0 < 169.0 (-25)	305.0 < 153.0 (-25)
77	Dichlorvos	3.98	220	$[M+H]^+$	221.0 < 109.0 (-17)	221.0 < 78.9 (-27)
78	Dicrotophos	3.1	237	$[M+H]^+$	238.0 < 72.0 (-30)	238.0 < 112.1 (-15)
79	Diethofencarb	5.18	267	$[M+H]^+$	268.0 < 124.0 (-35)	268.0 < 226.0 (-15)
80	Difenoconazole	7.18	405	$[M+H]^+$	406.0 < 250.9 (-30)	406.0 < 188.0 (-46)
81	Diflubenzuron	6.22	310	$[M+H]^+$	311.0 < 158.0 (-14)	311.0 < 141.0 (-30)
82	Diflufenican	7.4	394	$[M+H]^+$	395.0 < 265.9 (-25)	395.0 < 246.0 (-35)
83	Dimethachlor	4.9	255	$[M+H]^+$	256.0 < 224.0 (-20)	256.0 < 148.1 (-30)
84	Dimethametryn	6.29	255	$[M+H]^+$	256.0 < 186.0 (-25)	256.0 < 68.0 (-46)
85	Dimethenamid	5.39	275	$[M+H]^+$	276.0 < 244.0 (-20)	276.0 < 168.1 (-28)
86	Dimethoate	3.32	229	$[M+H]^+$	230.0 < 198.9 (-11)	230.0 < 125.0 (-22)
87	Dimethylvinphos	5.75	330	$[M+H]^+$	331.0 < 170.0 (-36)	331.0 < 127.0 (-13)
88	Diniconazole	7.15	325	$[M+H]^+$	326.0 < 70.1 (-25)	326.0 < 158.9 (-33)
89	Dinotefuran	2.93	202	$[M+H]^+$	202.6 < 129.1 (-12)	202.6 < 113.1 (-11)
90	Diphenamid	4.87	239	$[M+H]^+$	240.0 < 134.1 (-25)	240.0 < 167.1 (-22)
91	Dithiopyr	7.54	401	$[M+H]^+$	402.0 < 354.0 (-18)	402.0 < 271.9 (-32)
92	Diuron	4.78	232	$[M+H]^+$	233.0 < 72.0 (-25)	233.0 < 46.1 (-17)
93	Edifenphos	6.61	310	$[M+H]^+$	311.0 < 109.0 (-40)	311.0 < 282.9 (-18)
94	Emamectin B1a	7.88	885	$[M+H]^+$	886.5 < 158.1 (-36)	886.5 < 82.1 (-36)
95	Emamectin B1b	7.58	871	$[M+H]^+$	872.3 < 158.1 (-36)	872.3 < 82.1 (-55)
96	EPN	5.5	323	$[M+H]^+$	324.0 < 295.9 (-14)	324.0 < 156.9 (-22)

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
97	Epoxiconazole	6.05	329	$[M+H]^+$	330.0 < 121.0 (-21)	330.0 < 101.1 (-49)
98	Esprocarb	7.88	265	$[M+H]^+$	265.7 < 91.1 (-30)	265.7 < 71.1 (-16)
99	Ethaboxam	4.33	320	$[M+H]^+$	320.6 < 183.0 (-21)	320.6 < 200.0 (-25)
100	Ethametsulfuron-methyl	4.19	410	$[M+H]^+$	410.6 < 196.0 (-18)	410.6 < 168.0 (-30)
101	Ethiofencarb	4.34	225	$[M+H]^+$	225.6 < 107.1 (-16)	225.6 < 77.0 (-45)
102	Ethion	8.08	384	$[M+H]^+$	384.6 < 198.9 (-11)	384.6 < 143.0 (-24)
103	Ethoprophos	6.09	242	$[M+H]^+$	242.6 < 130.9 (-20)	242.6 < 173.0 (-14)
104	Ethoxyquin	5.2	217	$[M+H]^+$	218.0 < 174.1 (-27)	218.0 < 148.0 (-22)
105	Ethoxysulfuron	5.56	398	$[M+H]^+$	398.7 < 260.9 (-16)	398.7 < 218.0 (-25)
106	Etofenprox	9.65	376	$[M+NH_4]^+$	393.7 < 177.2 (-15)	393.7 < 359.2 (-12)
107	Etoxazole	8.49	359	$[M+H]^+$	359.6 < 141.0 (-29)	359.6 < 113.0 (-55)
108	Etrimfos	6.69	292	$[M+H]^+$	292.6 < 125.0 (-25)	292.6 < 265.0 (-17)
109	Famoxadone	6.74	374	$[M+NH_4]^+$	392.0 < 331.1 (-10)	392.0 < 238.0 (-17)
110	Fenamidone	5.3	311	$[M+H]^+$	311.7 < 92.1 (-24)	311.7 < 236.1 (-15)
111	Fenamiphos	6.27	303	$[M+H]^+$	303.6 < 217.0 (-23)	303.6 < 201.9 (-35)
112	Fenarimol	5.96	330	$[M+H]^+$	331.0 < 268.0 (-24)	331.0 < 81.1 (-32)
113	Fenazaquin	9.07	306	$[M+H]^+$	306.7 < 57.2 (-26)	306.7 < 161.2 (-17)
114	Fenbuconazole	6.12	337	$[M+H]^+$	336.9 < 125.0 (-31)	336.9 < 70.1 (-21)
115	Fenhexamid	5.9	301	$[M+H]^+$	302.0 < 97.2 (-24)	302.0 < 55.1 (-41)
116	Fenobucarb	5.17	207	$[M+H]^+$	207.9 < 95.0 (-16)	207.9 < 152.0 (-11)
117	Fenothiocarb	6.39	253	$[M+H]^+$	253.7 < 72.1 (-23)	253.7 < 160.0 (-10)
118	Fenoxanil	6.29	328	$[M+H]^+$	329.0 < 302.0 (-12)	329.0 < 86.1 (-23)
119	Fenoxaprop-p-ethyl	7.62	361	$[M+H]^+$	361.6 < 288.0 (-18)	361.6 < 119.1 (-26)
120	Fenoxycarb	6.33	301	$[M+H]^+$	302.1 < 88.1 (-21)	302.1 < 116.1 (-12)
121	Fenpropathrin	8.6	349	$[M+H]^+$	349.9 < 125.1 (-12)	349.9 < 55.1 (-44)
122	Fenpyroximate	8.71	421	$[M+H]^+$	421.6 < 366.1 (-16)	421.6 < 138.0 (-31)
123	Fenthion	6.65	278	$[M+H]^+$	279.0 < 169.0 (-18)	279.0 < 246.9 (-13)
124	Ferimzone	4.81	254	$[M+H]^+$	254.6 < 91.1 (-32)	254.6 < 132.1 (-20)
125	Fipronil	6.28	436	$[M-H]^-$	434.6 < 330.0 (16)	434.6 < 250.0 (26)
126	Fluacrypyrim	7.29	426	$[M+H]^+$	426.9 < 145.0 (-26)	426.9 < 205.0 (-11)
127	Fluazinam	8	464	$[M-H]^-$	462.7 < 416.0 (18)	462.7 < 398.0 (16)
128	Flubendiamide	6.43	682	$[M-H]^-$	680.7 < 254.1 (26)	680.7 < 274.1 (15)
129	Flucetosulfuron	5.25	487	$[M+H]^+$	487.8 < 156.0 (-20)	487.8 <273.0 (-26)
130	Fludioxonil	5.42	248	$[M-H]^-$	246.9 < 180.1 (26)	246.9 < 126.1 (30)
131	Flufenacet	6.01	363	$[M+H]^+$	363.6 < 152.1 (-20)	363.6 < 194.1 (-11)
132	Flufenoxuron	8.41	488	$[M+H]^+$	488.8 < 158.0 (-20)	488.8 < 141.0 (-46)
133	Flumiclorac-pentyl	7.81	423	$[M+NH_4]^+$	440.7 < 308.0 (-23)	440.7 < 354.0 (-16)
134	Fluopicolide	5.59	382	$[M+H]^+$	382.5 < 172.9 (-23)	382.5 < 145.0 (-48)
135	Fluopyram	5.86	396	$[M+H]^+$	396.5 < 173.0 (-28)	396.5 < 145.1 (-53)
136	Fluquinconazole	5.83	375	$[M+H]^+$	375.8 < 348.9 (-20)	375.8 < 306.9 (-26)
137	Flusilazole	6.26	315	$[M+H]^+$	315.6 < 247.0 (-18)	315.6 < 165.0 (-26)
138	Flusulfamide	6.89	414	$[M-H]^-$	412.6 < 171.1 (36)	412.6 < 349.0 (26)
139	Flutolanil	5.5	323	$[M+H]^+$	323.6 < 242.0 (-26)	323.6 < 262.0 (-19)
140	Fluvalinate	9.19	502	$[M+H]^+$	503.0 < 181.0 (-26)	503.0 < 208.0 (-14)
141	Fluxapyroxad	5.78	381	$[M+H]^+$	381.5 <362.0 (-15)	381.5 <341.9 (-21)
142	Fonofos	6.74	246	$[M+H]^+$	247.0 < 109.0 (-19)	247.0 < 137.0 (-12)
143	Forchlorfenuron	4.67	247	$[M-H]^-$	245.9 < 127.1 (11)	245.9 < 91.0 (26)
144	Fosthiazate	4.35	283	$[M+H]^+$	283.5 < 104.0 (-24)	283.5 < 227.9 (-10)
145	Furathiocarb	7.79	382	$[M+H]^+$	382.6 < 195.0 (-19)	382.6 < 252.0 (-13)

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
146	Halfenprox	9.99	476	$[M+H]^+$	494.0 < 183.0 (-20)	494.0 < 458.9 (-12)
147	Halosulfuron-methyl	5.85	434	$[M+H]^+$	434.8 < 182.0 (-22)	434.8 < 139.0 (-43)
148	Haloxyfop	6.4	361	$[M-H]^-$	359.9 < 288.0 (13)	359.9 < 196.0 (38)
149	Haloxyfop-R-Methyl	7.29	374	$[M+H]^+$	375.6 < 316.0 (-18)	375.6 < 91.1 (-32)
150	Hexaconazole	6.87	313	$[M+H]^+$	313.9 < 70.1 (-21)	313.9 < 158.9 (-32)
151	Hexaflumuron	7.43	460	$[M-H]^-$	458.8 < 438.9 (11)	458.8 < 175.1 (34)
152	Hexazinone	4.04	252	$[M+H]^+$	252.7 < 170.8 (-20)	252.7 < 71.1 (-32)
153	Hexythiazox	8.24	352	$[M+H]^+$	352.8 < 228.0 (-15)	352.8 < 168.1 (-25)
154	Imazalil	4.27	296	$[M+H]^+$	296.6 < 158.9 (-23)	296.6 < 200.9 (-18)
155	Imazamox	3.36	305	$[M-H]^-$	304.0 < 260.2 (12)	304.0 < 186.2 (32)
156	Imazapic	3.43	275	$[M+H]^+$	275.6 < 231.1 (-20)	275.6 < 163.0 (-26)
157	Imazaquin	3.94	311	$[M+H]^+$	311.6 < 267.0 (-21)	311.6 < 199.0 (-28)
158	Imazethapyr	3.74	289	$[M+H]^+$	289.6 < 245.1 (-21)	289.6 < 177.1 (-27)
159	Imazosulfuron	5.69	412	$[M+H]^+$	412.8 < 152.9 (-14)	412.8 < 156.0 (-19)
160	Imibenconazole	7.95	410	$[M+H]^+$	410.7 < 125.0 (-30)	410.7 < 171.0 (-20)
161	Imicyafos	3.7	304	$[M+H]^+$	304.5 < 201.0 (-22)	304.5 < 235.0 (-18)
162	Imidacloprid	3.17	255	$[M+H]^+$	255.8 < 209.0 (-16)	255.8 < 175.1 (-20)
163	Inabenfide	5.22	338	$[M-H]^-$	337.1 < 122.1 (15)	337.1 < 78.1 (34)
164	Indoxacarb	7.31	527	$[M+H]^+$	527.9 < 203.0 (-40)	527.9 < 150.0 (-24)
165	Iprobenfos	6.47	288	$[M+H]^+$	288.6 < 91.1 (-29)	288.6 < 205.0 (-11)
166	Iprovalicarb	5.93	320	$[M+H]^+$	320.8 < 119.0 (-20)	320.8 < 203.1 (-10)
167	Isazofos	5.8	313	$[M+H]^+$	313.7 < 162.0 (-16)	313.7 < 120.0 (-25)
168	Isoprocarb	4.58	193	$[M+H]^+$	193.9 < 95.1 (-15)	193.9 < 77.1 (-38)
169	Isoprothiolane	5.59	290	$[M+H]^+$	290.8 < 188.9 (-22)	290.8 < 231.0 (-12)
170	Isoproturon	4.69	206	$[M+H]^+$	206.7 < 72.1 (-21)	206.7 < 46.1 (-18)
171	Isopyrazam	7.23	359	$[M+H]^+$	359.7 < 244.1 (-23)	359.7 < 320.1 (-21)
172	Isoxathion	6.97	313	$[M+H]^+$	313.7 < 105.2 (-15)	313.7 < 286.0 (-10)
173	Kresoxim-methyl	6.51	313	$[M+H]^+$	314.1 < 222.0 (-14)	314.1 < 267.0 (-8)
174	Lactofen	7.85	461	$[M+NH_4]^+$	478.9 < 343.9 (-16)	478.9 < 222.9 (-34)
175	Lepimectin A3	9.30	705	$[M+NH_4]^+$	728.1 < 549.1 (-25)	728.1 < 181.2 (-37)
176	Lepimectin A4	9.59	719	$[M+Na]^+$	742.2 < 563.2 (-26)	742.2 < 195.0 (-37)
177	Linuron	5.26	248	$[M+H]^+$	249.0 < 160.0 (-18)	249.0 < 182.0 (-15)
178	Lufenuron	8.07	510	$[M-H]^-$	508.8 < 339.0 (12)	508.8 < 326.0 (17)
179	Malathion	5.55	330	$[M+H]^+$	330.8 < 99.0 (-23)	330.8 < 127.0 (-13)
180	Mandipropamid	5.38	411	$[M+H]^+$	411.9 < 328.0 (-16)	411.9 < 125.0 (-34)
181	Mecarbam	6.01	329	$[M+H]^+$	330.0 < 226.9 (-9)	330.0 < 97.0 (-38)
182	Mecoprop-P	5.32	214	$[M-H]^-$	213.0 < 141.1 (13)	213.0 < 105.0 (28)
183	Mefenacet	5.75	298	$[M+H]^+$	298.7 < 148.0 (-14)	298.7 < 120.1 (-24)
184	Mefenpyr-diethyl	6.86	372	$[M+H]^+$	372.8 < 327.0 (-16)	372.8 < 160.0 (-33)
185	Mepanipyrim	5.99	223	$[M+H]^+$	223.6 < 77.0 (-40)	223.6 < 106.1 (-26)
186	Metalaxyl	4.64	279	$[M+H]^+$	279.6 < 220.1 (-13)	279.6 < 192.1 (-17)
187	Metamifop	7.67	440	$[M+H]^+$	440.9 < 288.0 (-20)	440.9 < 123.1 (-28)
188	Metazosulfuron	5.46	475	$[M+H]^+$	475.9 < 182.0 (-20)	475.9 < 294.9 (-18)
189	Metconazole	6.88	319	$[M+H]^+$	320.1 < 70.0 (-24)	320.1 < 125.0 (-39)
190	Methabenzthiazuron	4.62	221	$[M+H]^+$	221.5 < 165.0 (-17)	221.5 < 150.0 (-31)
191	Methamidophos	1.27	141	$[M+H]^+$	142.0 < 94.0 (-18)	142.0 < 125.0 (-17)
192	Methidathion	4.88	302	$[M+H]^+$	302.9 < 145.0 (-10)	302.9 < 85.1 (-22)
193	Methiocarb	5.33	225	$[M+H]^+$	225.8 < 121.1 (-20)	225.8 < 169 (-10)
194	Methomyl	3.05	162	$[M+H]^+$	163.0 < 88.0 (-10)	163.0 < 106.1 (-11)

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
195	Methoxyfenozide	5.90	368	$[M+H]^+$	369.0 < 149.0 (-21)	369.0 < 313.1 (-8)
196	Metobromuron	4.55	258	$[M+H]^+$	258.5 < 169.9 (-19)	258.5 < 148.0 (-16)
197	Metolachlor	6.2	283	$[M+H]^+$	283.6 < 251.9 (-17)	283.6 < 176.1 (-25)
198	Metolcarb	3.83	165	$[M+H]^+$	165.9 < 109.1 (-12)	165.9 < 94.1 (-30)
199	Metominostrobin	4.79	284	$[M+H]^+$	284.6 < 196.0 (-18)	284.6 < 194.0 (-21)
200	Metrafenone	7.06	408	$[M+H]^+$	408.9 < 209.0 (-15)	408.9 < 226.9 (-22)
201	Metribuzin	4.1	214	$[M+H]^+$	215.1 < 187.1 (-19)	215.1 < 49.0 (-26)
202	Mevinphos	3.46	224	$[M+H]^+$	224.7 < 127.0 (-16)	224.7 < 193.0 (-9)
203	Milbemectin A3	9.35	535	$[M+H]^+$	510.9 < 493.2 (-12)	510.9 < 95.1 (-34)
204	Milbemectin A4	9.70	543	$[M+H]^+$	525.0 < 109.2 (-27)	525.0 < 507.2 (-13)
205	Molinate	6.36	187	$[M+NH_4]^+$	204.6 < 145.1 (-15)	204.6 < 115.0 (-26)
206	Monocrotophos	3.06	223	$[M+H]^+$	223.6 < 127.0 (-15)	223.6 < 193.0 (-8)
207	Myclobutanil	5.64	288	$[M+H]^+$	289.1 < 70.1 (-21)	289.1 < 125.0 (-32)
208	Napropamide	6.07	271	$[M+H]^+$	271.7 < 171.1 (-19)	271.7 < 129.1 (-16)
209	Nicosulfuron	3.95	410	$[M+H]^+$	410.9 < 182.0 (-19)	410.9 < 213.0 (-17)
210	Novaluron	7.52	492	$[M+H]^+$	492.8 < 158.0 (-18)	492.8 < 140.9 (-40)
211	Nuarimol	5.21	314	$[M+H]^+$	315.0 < 252.0 (-22)	315.0 < 81.1 (-30)
212	Ofurace	3.96	281	$[M+H]^+$	281.6 < 254.1 (-12)	281.6 < 160.1 (-24)
213	Omethoate	2.9	213	$[M+H]^+$	213.5 < 125.0 (-21)	213.5 < 183.0 (-11)
214	Orysastrobin	5.56	391	$[M+H]^+$	392.1 < 205.0 (-15)	392.1 < 116.1 (-28)
215	Oxadiazon	8.01	344	$[M+H]^+$	344.9 < 303.0 (-14)	344.9 < 219.9 (-19)
216	Oxadixyl	3.64	278	$[M+H]^+$	278.6 < 219.1 (-12)	278.6 < 132.1 (-29)
217	Oxamyl	2.96	219	$[M+NH_4]^+$	236.8 < 72.1 (-25)	236.8 < 90.1 (-8)
218	Oxaziclomefone	7.7	375	$[M+H]^+$	375.8 < 190.1 (-15)	375.8 < 161.0 (-28)
219	Oxydemeton-methyl	2.99	246	$[M+H]^+$	246.5 < 169.0 (-13)	246.5 < 109.0 (-27)
220	Paclobutrazol	5.5	293	$[M+H]^+$	294.1 < 70.1 (-21)	294.1 < 125.1 (-38)
221	Pebulate	7.21	203	$[M+H]^+$	204.1 < 128.1 (-12)	204.1 < 57.1 (-17)
222	Penconazole	6.55	283	$[M+H]^+$	284.0 < 70.1 (-16)	284.0 < 159.0 (-30)
223	Pencycuron	7.14	328	$[M+H]^+$	328.5 < 125.0 (-23)	328.5 < 218.0 (-15)
224	Pendimethalin	8.31	281	$[M+H]^+$	282.1 < 212.0 (-12)	282.1 < 194.0 (-18)
225	Penoxsulam	4.11	483	$[M+H]^+$	483.9 < 195.0 (-28)	483.9 < 164.0 (-34)
226	Penthiopyrad	6.53	359	$[M+H]^+$	359.8 < 276.0 (-15)	359.8 < 177.0 (-34)
227	Phenmedipham	4.86	300	$[M+NH_4]^+$	318.1 < 136.0 (-24)	318.1 < 168.0 (-14)
228	Phenothrin	9.44	350	$[M+H]^+$	351.0 < 183.1 (-19)	351.0 < 249.1 (-19)
229	Phenthoate	6.44	320	$[M+H]^+$	321.0 < 79.0 (-43)	321.0 < 247.0 (-12)
230	Phorate	7.02	260	$[M+H]^+$	260.8 < 75.0 (-11)	260.8 < 47.0 (-34)
231	Phosalone	6.97	367	$[M+H]^+$	367.7 < 182.0 (-17)	367.7 < 111.0 (-40)
232	Phosmet	5	317	$[M+H]^+$	317.8 < 160.0 (-16)	317.8 < 77.0 (-54)
233	Phosphamidon	3.73	299	$[M+H]^+$	300.0 < 174.0 (-14)	300.0 < 127.0 (-30)
234	Phoxim	6.95	298	$[M+H]^+$	298.5 < 77.0 (-30)	298.5 < 129.0 (-11)
235	Picolinafen	7.96	376	$[M+H]^+$	376.9 < 237.9 (-27)	376.9 < 358.9 (-20)
236	Picoxystrobin	6.36	367	$[M+H]^+$	367.9 < 145.0 (-21)	367.9 < 205.1 (-9)
237	Piperophos	7.34	353	$[M+H]^+$	353.7 < 170.9 (-23)	353.7 < 255.0 (-14)
238	Pirimicarb	4.11	238	$[M+H]^+$	238.8 < 72.1 (-23)	238.8 < 182.1 (-16)
239	Pirimiphos-ethyl	7.97	333	$[M+H]^+$	333.6 < 198.1 (-23)	333.6 < 182.1 (-23)
240	Pirimiphos-methyl	7.02	305	$[M+H]^+$	305.7 < 108.0 (-31)	305.7 < 164.1 (-22)
241	Pretilachlor	7.53	311	$[M+H]^+$	312.1 < 252.0 (-17)	312.1 < 176.1 (-29)
242	Probenazole	3.94	223	$[M+H]^+$	224.0 < 41.0 (-22)	224.0 < 39.0 (-45)
243	Prochloraz	6.86	375	$[M+H]^+$	375.8 < 308.0 (-13)	375.8 < 70.1 (-26)

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
244	Profenofos	7.69	374	$[M+H]^+$	374.8 < 304.8 (-18)	374.8 < 346.8 (-17)
245	Promecarb	5.51	207	$[M+H]^+$	208.1 < 109.0 (-16)	208.1 < 151.1 (-10)
246	Prometryn	5.7	241	$[M+H]^+$	241.6 < 158.0 (-23)	241.6 < 200.1 (-18)
247	Propachlor	4.69	211	$[M+H]^+$	211.7 < 170.0 (-15)	211.7 < 94.1 (-27)
248	Propamocarb	2.91	188	$[M+H]^+$	188.7 < 102.1 (-20)	188.7 < 74.0 (-25)
249	Propanil	5.34	217	$[M-H]^-$	215.9 < 160.0 (16)	215.9 < 124.0 (23)
250	Propaquizafop	7.86	443	$[M+H]^+$	443.7 < 100.1 (-21)	443.7 < 299.0 (-23)
251	Propazine	5.36	229	$[M+H]^+$	229.7 < 146.0 (-23)	229.7 < 188.0 (-17)
252	Propiconazole	6.75	341	$[M+H]^+$	342.0 < 158.9 (-28)	342.0 < 69.2 (-21)
253	Propisochlor	6.69	283	$[M+H]^+$	283.9 < 224.0 (-11)	283.9 < 43.1 (-25)
254	Propoxur	3.99	209	$[M+H]^+$	209.8 < 111.0 (-14)	209.8 < 93.0 (-25)
255	Propyzamide	5.66	255	$[M+H]^+$	256.0 < 189.9 (-14)	256.0 < 172.9 (-23)
256	Prothiofos	9.14	344	$[M+H]^+$	344.9 < 240.7 (-20)	344.9 < 268.8 (-12)
257	Pymetrozine	3.98	217	$[M+H]^+$	218.0 < 104.6 (-25)	218.0 < 78.1 (-42)
258	Pyraclofos	6.95	360	$[M+H]^+$	360.5 < 256.9 (-23)	360.5 < 138.0 (-40)
259	Pyraclostrobin	6.89	387	$[M+H]^+$	388.0 < 194.1 (-13)	388.0 < 163.1 (-25)
260	Pyrazolynate	7.06	438	$[M+H]^+$	438.6 < 91.1 (-37)	438.6 < 172.9 (-20)
261	Pyrazophos	7.04	373	$[M+H]^+$	373.5 < 222.0 (-21)	373.5 < 194.0 (-32)
262	Pyrazoxyfen	6.66	402	$[M+H]^+$	402.9 < 91.1 (-40)	402.9 < 105.1 (-21)
263	Pyribenzoxim	7.89	609	$[M+Na]^+$	631.8 < 488.1 (-21)	631.8 < 180.1 (-40)
264	Pyributicarb	8.15	330	$[M+H]^+$	330.6 < 181.0 (-16)	330.6 < 108.1 (-28)
265	Pyridaben	9.01	364	$[M+H]^+$	364.6 < 147.1 (-25)	364.6 < 309.0 (-14)
266	Pyridaphenthion	5.7	340	$[M+H]^+$	340.5 < 189.0 (-21)	340.5 < 205.0 (-22)
267	Pyridate	9.56	378	$[M+H]^+$	378.8 < 207.0 (-21)	378.8 < 351.0 (-10)
268	Pyrifluquinazon	5.75	464	$[M+H]^+$	464.9 < 423.0 (-22)	464.9 < 92.1 (-37)
269	Pyrimethanil	5.26	199	$[M+H]^+$	199.6 < 107.1 (-24)	199.6 < 82.1 (-26)
270	Pyrimidifen	7.93	377	$[M+H]^+$	377.6 < 184.1 (-24)	377.6 < 150.1 (-37)
271	Pyriminobac-methyl E	5.44	361	$[M+H]^+$	361.6 < 330.0 (-14)	361.6 < 284.0 (-30)
272	Pyriminobac-methyl Z	5.03	361	$[M+H]^+$	361.6 < 330.0 (-15)	361.6 < 244.0 (-26)
273	Pyrimisulfan	4.73	419	$[M+H]^+$	419.5 < 370.0 (-19)	419.5 < 255.0 (-28)
274	Pyriproxyfen	8.12	321	$[M+H]^+$	321.6 < 96.1 (-16)	321.6 < 78.0 (-53)
275	Pyroquilon	3.96	173	$[M+H]^+$	173.8 < 117.1 (-31)	173.8 < 132.1 (-22)
276	Quinoclamine	3.91	207	$[M+H]^+$	208.0 < 105.1 (-25)	208.0 < 77.0 (-38)
277	Rimsulfuron	4.27	431	$[M+H]^+$	431.5 < 182.0 (-22)	431.5 < 325.00 (-16)
278	Saflufenacil	4.95	500	$[M+H]^+$	500.8 < 197.9 (-45)	500.8 < 348.9 (-29)
279	Sethoxydim	7.9	327	$[M+H]^+$	327.6 < 178.0 (-20)	327.6 < 282.1 (-12)
280	Simazine	4.13	201	$[M+H]^+$	201.9 < 104.0 (-26)	201.9 < 124.1 (-20)
281	Simeconazole	5.98	293	$[M+H]^+$	294.1 < 70.1 (-21)	294.1 < 135.0 (-21)
282	Simetryn	4.36	213	$[M+H]^+$	213.6 < 68.0 (-36)	213.6 < 124.1 (-20)
283	Spinetoram (XDE-175-J)	7.27	748	$[M+H]^+$	748.1 < 142.1 (-32)	748.1 < 98.1 (-55)
284	Spinetoram (XDE-175-L)	7.7	760	$[M+H]^+$	760.1 < 142.1 (-31)	760.1 < 98.1 (-55)
285	Spinosyn A	6.76	732	$[M+H]^+$	732.0 < 142.1 (-30)	732.0 < 98.1 (-54)
286	Spinosyn D	7.21	746	$[M+H]^+$	746.3 < 142.1 (-31)	746.3 < 98.1 (-55)
287	Spirotetramat	5.91	373	$[M+H]^+$	373.6 < 216.1 (-34)	373.6 < 302.1 (-17)
288	Sulfoxaflor	3.35	277	$[M+H]^+$	278.0 < 174.0 (-12)	278.0 < 154.0 (-29)
289	Sulprofos	8.31	322	$[M+H]^+$	322.5 < 218.9 (-16)	322.5 < 155.0 (-24)
290	TCMTB	5.27	238	$[M+H]^+$	238.8 < 180.0 (-12)	238.8 < 136.1 (-26)
291	Tebuconazole	6.59	307	$[M+H]^+$	308.1 < 70.1 (-22)	308.1 < 125.1 (-40)
292	Tebufenozide	6.37	352	$[M+H]^+$	353.2 < 133.1 (-20)	353.2 < 297.1 (-10)

No.	Compounds	t_R (min)	M.W	Ionization	Precursor ion > Product ion (CE, V)	
					Quantifier	Qualifier
293	Tebufenpyrad	7.84	333	$[M+H]^+$	333.7 < 117.0 (-38)	333.7 < 145.0 (-27)
294	Tebupirimfos	7.99	318	$[M+H]^+$	318.6 < 153.1 (-30)	318.6 < 277.0 (-15)
295	Teflubenzuron	7.95	380	$[M-H]^-$	379.1 < 339.0 (11)	379.1 < 196.0 (22)
296	Terbuthylazine	5.49	229	$[M+H]^+$	229.7 < 174.0 (-17)	229.7 < 104.0 (-31)
297	Terbutryn	5.8	241	$[M+H]^+$	241.6 < 186.1 (-19)	241.6 < 68.0 (-42)
298	Tetrachlorvinphos	6.38	366	$[M+H]^+$	366.7 < 127.0 (-14)	366.7 < 205.9 (-38)
299	Tetraconazole	5.97	372	$[M+H]^+$	371.8 < 159.0 (-30)	371.8 < 70.1 (-23)
300	Thenylchlor	6	324	$[M+H]^+$	323.8 < 127.0 (-15)	323.8 < 53.0 (-55)
301	Thiabendazole	3.33	201	$[M+H]^+$	201.5 < 175.0 (-24)	201.5 < 131.1 (-31)
302	Thiacloprid	3.4	252	$[M+H]^+$	252.6 < 126.0 (-21)	252.6 < 99.0 (-43)
303	Thiamethoxam	3.05	291	$[M+H]^+$	291.7 < 211.0 (-13)	291.7 < 181.0 (-22)
304	Thiazopyr	6.6	396	$[M+H]^+$	396.6 < 377.0 (-23)	396.6 < 334.9 (-29)
305	Thidiazuron	3.95	220	$[M-H]^-$	218.9 < 100.0 (9)	218.9 < 71.0 (32)
306	Thifensulfuron-methyl	3.78	387	$[M+H]^+$	387.8 < 167.1 (-17)	387.8 < 204.9 (-27)
307	Thifluzamide	6.14	528	$[M-H]^-$	526.6 < 125.0 (48)	526.6 < 166.1 (23)
308	Thiobencarb	7.09	257	$[M+H]^+$	257.8 < 125.0 (-20)	257.8 < 89.0 (-48)
309	Thiodicarb	4.22	354	$[M+H]^+$	355.0 < 88.0 (-21)	355.0 < 108.0 (-15)
310	Thiophanate-methyl	3.86	342	$[M+H]^+$	342.8 < 151.0 (-20)	342.8 < 310.9 (-11)
311	Tiadinil	5.77	267	$[M-H]^-$	266.2 < 71.0 (22)	266.2 < 238.1 (10)
312	Tolclofos-methyl	7.03	300	$[M+H]^+$	300.9 < 125.0 (-20)	300.9 < 268.9 (-16)
313	Tolfenpyrad	7.95	383	$[M+H]^+$	383.7 < 197.0 (-25)	383.7 < 154.1 (-42)
314	Triadimefon	5.65	293	$[M+H]^+$	294.0 < 197.0 (-16)	294.0 < 69.1 (-22)
315	Triadimenol	5.8	295	$[M+H]^+$	296.0 < 70.0 (-12)	296.0 < 99.0 (-16)
316	Tri-allate	8.33	303	$[M+H]^+$	303.7 < 86.1 (-17)	303.7 < 142.9 (-27)
317	Triazophos	5.8	313	$[M+H]^+$	313.5 < 162.0 (-19)	313.5 < 119.1 (-34)
318	Tribenuron-methyl	4.48	395	$[M+H]^+$	395.8 < 155.0 (-15)	395.8 < 181.0 (-21)
319	Tribufos	9.03	314	$[M+H]^+$	314.9 < 169.0 (-17)	314.9 < 57.2 (-25)
320	Trichlorfon	3.33	256	$[M+H]^+$	256.9 < 109.1 (-18)	256.9 < 221 (-11)
321	Triclopyr	3.17	255	$[M+H]^+$	255.9 < 209.8 (-15)	255.9 < 145.7 (-26)
322	Tricyclazole	3.57	189	$[M+H]^+$	189.5 < 136.0 (-27)	189.5 < 163.0 (-22)
323	Trifloxystrobin	7.39	408	$[M+H]^+$	408.6 < 186.0 (-19)	408.6 < 145.0 (-43)
324	Triflumizole	7.45	345	$[M+H]^+$	346.0 < 277.9 (-11)	346.0 < 43.1 (-28)
325	Triflumuron	6.91	358	$[M+H]^+$	358.8 < 156.0 (-18)	358.8 < 139.0 (-30)
326	Trimethacarb	4.76	193	$[M+H]^+$	193.7 < 137.1 (-12)	193.7 < 122.0 (-25)
327	Triticonazole	5.96	317	$[M+H]^+$	318.1 < 70.0 (-22)	318.1 < 125.0 (-37)
328	Uniconazole	5.61	291	$[M+H]^+$	291.9 < 70.1 (-24)	291.9 < 125.0 (-32)
329	Vamidothion	3.24	287	$[M+H]^+$	287.7 < 145.8 (-18)	287.7 < 118.0 (-23)
330	Vernolate	7.21	203	$[M+H]^+$	204.1 < 128.1 (-13)	204.1 < 43.1 (-21)
331	XMC	4.38	179	$[M+H]^+$	180.1 < 123.1 (-12)	180.1 < 108.1 (-27)
332	Zoxamide	6.78	335	$[M+H]^+$	335.8 < 186.9 (-22)	335.8 < 159.0 (-40)

Table S5. Validation results including limit of quantitation (LOQ), linearity (r^2), and recoveries (average and relative standard deviations, RSD) of 332 target analytes in each crop (brown rice, orange, and spinach)

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g)		50 (ng/g)		r^2	10 (ng/g)		50 (ng/g)		r^2	10 (ng/g)		50 (ng/g)	
				Rec.,%	RSD, %	Rec.,%	RSD, %		Rec.,%	RSD, %	Rec.,%	RSD, %		Rec.,%	RSD, %	Rec.,%	RSD, %
1	2,4-D	4	0.999	9.5	244.9	13.7	8.3	0.992	-	-	18.5	36.3	0.999	2.9	156.6	8.8	17.6
2	Abamectin B1a	1	0.995	69.3	155.7	93.6	7.2	1.000	-	-	95.9	19.1	1.000	0.0	-	93.0	15.2
3	Acephate	1	0.991	75.9	14.2	75.0	8.4	1.000	57.8	32.1	70.7	9.8	0.995	57.3	15.7	81.8	4.8
4	Acetamiprid	1	0.999	79.5	7.6	95.4	5.9	0.999	83.9	9.1	89.6	13.3	1.000	102.0	4.5	96.0	3.6
5	Acibenzolar-S-methyl	2	0.999	51.8	41.4	97.3	6.6	0.999	95.5	16.2	92.7	4.1	0.999	61.6	31.5	73.6	6.2
6	Alachlor	1	0.997	89.6	9.4	98.4	4.1	0.997	70.0	9.2	101.5	2.4	0.998	81.5	8.6	95.5	4.5
7	Aldicarb	1	0.995	6.4	244.9	98.7	25.7	1.000	-	-	102.3	30.2	0.998	33.8	63.0	104.5	26.8
8	Allidochlor	1	0.999	85.6	12.1	101.3	2.4	0.999	87.9	9.8	98.2	4.9	0.997	98.5	7.5	105.1	2.7
9	Ametoctradin	1	0.999	81.6	11.3	97.0	4.8	0.998	78.8	5.1	92.4	4.9	0.997	86.5	6.8	91.4	3.7
10	Ametryn	1	1.000	106.1	2.3	98.0	5.7	0.999	112.3	5.8	98.9	2.2	1.000	102.0	5.9	99.1	3.1
11	Amisulbrom	1	1.000	74.2	19.4	100.6	11.8	1.000	122.6	5.9	105.0	6.3	0.999	119.8	10.4	93.5	7.1
12	Amitraz	1	0.998	28.4	19.5	22.2	4.9	1.000	32.9	5.0	14.8	11.6	0.996	55.5	10.5	22.1	6.6
13	Anilofos	1	0.996	90.2	6.2	100.7	5.6	0.999	97.7	6.3	94.2	5.6	0.997	74.9	7.2	95.7	5.3
14	Asulam	1	0.992	27.1	30.8	45.1	7.8	0.995	93.8	13.2	76.1	7.5	1.000	8.3	65.3	24.4	11.3
15	Atrazine	20	0.996	81.6	7.9	101.1	4.1	1.000	92.6	9.2	96.6	1.9	0.990	65.8	5.5	101.2	2.0
16	Azaconazole	1	0.991	74.7	4.4	101.3	2.2	0.995	73.1	13.8	99.0	4.9	0.999	78.9	10.3	99.0	3.9
17	Azamethiphos	1	0.996	84.8	5.1	94.3	3.2	1.000	96.7	3.3	98.3	4.8	0.999	83.9	4.9	96.2	2.3
18	Azimsulfuron	1	0.997	66.8	12.7	70.6	4.2	0.999	92.6	7.2	85.9	6.7	0.999	52.2	12.0	77.8	4.3
19	Azinphos-methyl	1	0.996	124.2	9.2	110.5	4.9	0.991	87.8	24.2	93.8	10.7	0.999	94.0	13.5	106.5	5.1
20	Azoxystrobin	5	1.000	104.2	7.0	105.6	5.6	1.000	96.2	8.3	91.8	4.8	1.000	103.8	6.7	100.0	3.0
21	Bendiocarb	1	0.995	75.8	9.0	102.8	2.0	0.996	85.7	6.5	99.3	5.7	0.999	81.9	4.4	101.4	2.2
22	Bensulfuron-methyl	1	0.993	63.1	9.7	78.6	6.3	0.998	86.6	15.6	93.0	2.0	1.000	75.2	4.6	81.5	2.7
23	Bensulide	1	0.998	82.8	18.6	118.2	10.0	0.996	107.2	13.7	100.2	1.9	0.994	68.5	11.2	100.3	5.3
24	Bentazone	1	0.991	86.7	4.8	100.5	3.2	0.993	72.9	8.9	100.0	4.6	0.990	78.3	4.3	103.6	1.4
25	Benthiavalicarb-isopropyl	1	0.999	122.6	11.1	108.0	5.8	0.992	94.4	36.3	113.4	10.9	0.996	85.5	8.6	98.7	5.5
26	Benzobicyclon	1	0.997	91.9	15.5	108.7	5.5	1.000	116.0	18.1	92.0	8.3	0.997	88.7	16.0	90.3	9.0
27	Benzoximate	1	0.995	96.4	21.3	117.1	7.7	0.987	47.2	31.2	107.4	7.1	0.986	75.5	26.6	107.2	5.2
28	Bifenazate	1	0.996	-	-	60.6	8.4	0.987	94.6	29.4	107.9	7.7	0.991	-	-	20.2	18.3
29	Bromacil	1	0.996	87.5	6.7	113.7	4.0	1.000	93.4	12.1	98.9	3.6	0.997	84.5	11.6	105.1	2.9
30	Bromobutide	1	0.999	85.1	5.7	100.7	3.5	1.000	90.7	6.0	100.8	2.8	0.999	90.5	10.7	99.7	4.7
31	Bromoxynil	1	0.993	55.5	23.4	70.8	18.2	0.999	82.4	12.6	80.8	9.5	0.998	54.5	31.3	64.2	9.8
32	Bupirimate	1	1.000	112.4	11.9	120.8	6.4	0.996	102.0	12.5	87.6	6.0	0.998	89.4	7.7	98.0	8.4

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
33	Buprofezin	1	0.999	86.5	8.0	100.8	4.0	1.000	90.6	2.4	98.0	1.8	1.000	90.2	8.8	94.7	1.6
34	Butachlor	1	0.999	107.5	7.7	101.7	4.0	0.999	112.6	4.5	103.7	2.9	1.000	89.7	7.9	93.1	5.7
35	Butafenacil	1	1.000	101.4	13.7	116.1	7.5	0.994	128.0	3.0	101.6	10.6	0.999	87.0	13.0	99.2	9.5
36	Butocarboxim	5	0.995	72.2	12.3	102.4	2.6	0.921	78.2	37.7	110.4	17.5	0.997	91.8	19.0	100.7	8.6
37	Cadusafos	1	0.992	79.3	11.6	95.3	4.6	0.998	94.0	6.5	102.3	2.8	0.993	78.9	9.3	100.8	5.0
38	Carbaryl	1	0.993	103.0	5.0	109.4	2.9	1.000	89.5	9.5	100.8	7.0	0.998	90.5	8.2	104.9	2.5
39	Carbendazim	1	0.992	98.5	2.7	90.5	2.6	1.000	70.8	6.1	77.6	7.6	0.998	74.8	3.4	92.2	2.0
40	Carbofuran	1	0.994	105.7	3.4	138.7	2.8	0.998	112.7	2.7	122.7	5.8	0.995	89.4	6.7	122.6	3.0
41	Carbophenothion	1	0.999	81.3	8.8	94.9	2.2	0.999	105.4	4.4	104.3	2.7	1.000	104.0	6.5	94.0	3.8
42	Carboxin	1	0.992	76.8	7.0	99.1	1.9	1.000	94.0	6.1	94.9	6.1	0.993	63.7	6.1	100.4	3.5
43	Carfentrazone-ethyl	2	0.990	83.6	11.6	112.0	6.7	0.998	105.1	26.3	109.4	4.5	0.998	76.2	17.7	103.1	9.3
44	Carpropamid	1	0.994	99.6	6.7	115.5	4.8	1.000	114.3	5.4	93.8	3.0	0.996	99.5	6.6	89.4	4.8
45	Chinomethionat	5	0.996	33.8	47.5	63.7	15.8	0.998	82.6	15.6	86.3	5.3	0.998	50.0	45.0	70.9	5.5
46	Chlorantraniliprole	1	0.993	76.3	14.3	93.4	15.0	0.999	87.1	29.1	94.5	8.2	0.999	98.5	7.8	93.2	6.9
47	Chlorfenvinphos	1	0.991	107.6	12.1	112.3	7.7	1.000	105.5	11.0	92.7	2.9	0.998	70.6	12.6	94.4	5.9
48	Chlorfluazuron	1	1.000	111.9	5.1	101.0	6.4	1.000	100.2	4.4	90.1	2.9	0.999	90.8	5.2	102.7	4.6
49	Chloridazon	1	0.999	103.6	8.6	101.5	6.2	0.998	91.7	9.7	88.6	11.6	0.999	94.2	11.5	102.1	6.5
50	Chlorimuron-ethyl	1	0.992	70.0	11.8	69.4	6.5	0.999	75.0	12.3	80.9	8.5	0.993	42.7	18.1	72.4	6.4
51	Chlorotoluron	1	0.998	79.0	4.0	94.6	4.5	1.000	96.4	7.4	94.9	3.9	0.999	93.9	4.6	97.8	2.1
52	Chlorpyrifos	1	0.999	105.3	9.6	102.1	4.3	1.000	98.0	5.5	100.6	1.8	1.000	95.8	2.7	91.1	4.0
53	Chlorpyrifos-methyl	5	0.996	103.4	12.1	99.4	10.6	0.990	81.7	16.6	96.2	4.7	0.998	99.2	14.8	103.1	9.6
54	Chlorsulfuron	1	0.997	26.5	25.9	54.2	7.3	0.995	48.7	6.5	77.3	5.0	0.990	-	-	58.6	6.1
55	Chromafenozide	1	0.998	118.0	15.0	101.1	5.7	0.998	94.9	24.0	90.4	8.3	0.997	87.9	12.2	102.4	3.1
56	Clethodim	5	1.000	109.4	6.5	103.5	5.9	0.997	96.2	11.8	92.3	7.8	1.000	91.2	12.5	82.4	3.5
57	Clofentezine	1	0.997	98.7	9.6	112.1	3.3	0.995	76.4	13.3	105.4	3.1	0.993	81.7	6.1	103.6	3.7
58	Clomazone	1	0.996	76.9	8.6	100.2	4.7	0.996	92.2	10.2	100.6	5.7	0.999	77.9	8.6	99.5	2.4
59	Clomeprop	1	0.997	81.6	9.6	104.3	3.7	0.989	95.5	6.6	102.9	4.5	1.000	91.7	2.7	102.9	4.7
60	Clothianidin	1	0.992	88.7	9.1	103.0	4.1	0.991	115.4	12.7	108.1	18.6	0.999	97.6	15.3	100.1	6.1
61	Cyanazine	1	0.995	91.9	7.9	102.5	3.6	1.000	88.6	5.3	100.9	3.0	0.999	93.5	5.1	108.5	1.2
62	Cyazofamid	1	0.998	101.4	11.2	113.1	4.0	0.998	84.0	11.2	99.5	3.7	0.982	78.8	6.5	108.7	3.9
63	Cycloate	2	0.993	87.9	20.6	94.5	7.2	0.996	102.1	13.8	99.2	4.4	1.000	107.6	12.1	100.1	5.2
64	Cycloprothrin	10	0.998	102.7	13.4	102.6	12.0	0.995	111.0	14.8	97.6	6.2	0.999	102.7	13.3	91.5	4.0
65	Cyclosulfamuron	1	0.996	58.4	9.6	74.6	5.2	0.999	82.3	12.0	91.4	5.7	0.992	55.7	14.6	81.0	2.3
66	Cyflufenamid	1	0.994	73.9	8.7	101.2	6.6	0.997	75.8	8.2	105.2	3.7	0.999	92.1	13.4	100.6	4.5
67	Cymoxanil	1	0.997	109.6	10.2	109.7	3.5	0.998	79.3	10.6	100.0	6.2	0.998	132.2	8.5	103.2	4.6
68	Cyproconazole	1	0.992	104.7	13.3	107.7	4.7	0.999	119.3	17.7	102.1	9.6	0.994	93.4	10.5	98.7	3.2
69	Cyprodinil	1	0.992	70.5	29.2	97.9	6.8	0.999	46.6	34.5	98.0	4.5	0.994	132.2	8.5	103.2	4.6

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
70	Cyromazine	10	0.998	22.2	20.2	35.0	5.2	1.000	0.0	-	10.1	78.5	0.999	33.8	9.0	40.6	4.2
71	Daimuron	1	0.988	94.8	3.8	101.8	4.8	0.997	87.4	12.8	106.9	8.2	0.997	83.9	3.7	101.6	1.5
72	Deltamethrin	2	0.998	79.2	11.6	119.6	3.8	0.999	110.3	10.3	98.4	2.1	1.000	111.8	13.3	103.8	3.1
73	Demeton-S-Methyl	10	0.996	56.4	27.7	110.2	14.8	0.991	44.1	66.1	93.2	12.3	0.976	31.8	46.9	102.5	10.8
74	Diafenthiuron	1	0.991	72.3	12.2	73.4	6.1	0.999	78.2	14.2	68.7	9.2	0.998	0.0	-	22.7	12.1
75	Di-allate	2	0.998	112.7	6.8	107.4	3.0	1.000	92.3	4.6	100.0	6.4	1.000	77.8	10.0	98.0	6.3
76	Diazinon	1	0.996	95.0	7.8	103.0	4.8	1.000	97.2	7.1	102.8	2.0	1.000	96.5	5.7	100.8	3.1
77	Dichlorvos	2	0.995	106.4	11.4	86.3	5.6	0.999	-	-	80.7	12.6	0.999	84.5	11.0	97.5	6.3
78	Dicrotophos	1	1.000	91.4	4.3	94.6	3.7	1.000	90.4	5.9	95.2	8.1	1.000	89.2	5.0	95.1	2.6
79	Diethofencarb	1	0.997	96.6	3.9	103.0	3.2	0.999	109.1	7.1	98.3	4.4	1.000	94.9	6.5	97.0	3.0
80	Difenoconazole	1	0.999	109.8	7.9	103.3	2.0	0.999	97.9	4.6	96.2	2.4	1.000	101.6	3.7	101.5	3.5
81	Diflubenzuron	1	1.000	128.1	12.9	117.3	6.6	0.995	104.0	14.1	108.2	6.0	0.999	78.7	9.8	102.2	5.1
82	Diflufenican	1	0.999	113.8	7.7	104.6	4.0	1.000	99.1	7.9	100.6	3.0	0.998	86.8	3.2	100.2	1.6
83	Dimethachlor	1	0.992	90.2	6.4	103.4	4.4	0.999	91.1	6.8	101.8	2.7	0.999	81.6	8.0	103.4	3.8
84	Dimethametryn	1	0.999	89.0	3.7	97.3	4.6	1.000	91.0	2.1	100.0	1.9	0.998	84.3	5.5	96.6	1.9
85	Dimethenamid	1	0.996	92.3	6.1	111.6	5.1	0.999	97.2	6.4	91.9	2.2	0.997	73.9	5.1	101.9	1.4
86	Dimethoate	1	0.994	92.8	4.7	96.6	3.7	0.998	89.9	5.4	96.8	6.2	1.000	93.5	4.6	100.4	1.4
87	Dimethylvinphos	1	0.992	88.9	18.0	114.0	3.7	0.999	114.9	14.2	98.7	6.4	0.996	81.0	9.6	105.5	6.3
88	Diniconazole	1	0.998	97.4	7.0	104.4	4.2	0.999	83.1	8.0	97.9	2.8	0.998	91.3	11.5	102.1	4.3
89	Dinotefuran	2	0.995	77.8	7.2	97.7	2.8	0.999	78.3	11.2	77.0	14.5	1.000	90.2	3.9	94.4	4.5
90	Diphenamid	1	0.996	82.8	4.1	101.0	2.9	1.000	103.9	2.0	100.6	3.0	0.999	91.1	7.1	100.4	4.7
91	Dithiopyr	1	0.999	91.2	12.8	109.0	4.4	0.999	93.7	7.2	101.0	2.3	1.000	94.8	6.5	97.8	2.4
92	Diuron	1	0.990	90.5	7.2	102.7	3.6	0.999	92.8	8.2	96.8	3.9	0.995	72.0	11.1	103.3	4.4
93	Edifenphos	1	0.996	91.6	5.6	109.1	4.0	0.997	85.4	6.8	104.2	3.7	0.998	85.5	8.0	108.1	2.9
94	Emamectin B1a	1	1.000	97.0	3.3	102.7	2.3	1.000	96.0	2.8	92.1	2.2	1.000	100.1	2.9	95.9	1.7
95	Emamectin B1b	5	1.000	111.7	14.3	96.5	9.1	0.996	97.7	13.8	86.7	3.7	1.000	90.5	13.5	91.5	4.2
96	EPN	1	0.994	97.2	2.6	108.5	3.5	0.999	99.7	4.3	100.7	2.1	0.996	79.3	4.6	102.8	2.2
97	Epoxiconazole	1	0.999	89.4	8.8	111.6	2.9	0.998	97.9	7.1	101.2	2.2	0.994	79.7	5.1	103.0	1.4
98	Esprocarb	1	0.993	89.4	7.9	97.5	3.0	0.997	84.7	6.4	105.9	3.6	0.999	83.5	6.5	96.0	1.5
99	Ethaboxam (EBX)	1	0.995	72.3	12.0	108.2	6.1	0.999	100.3	7.6	96.1	2.8	0.998	95.5	7.7	98.0	2.5
100	Ethametsulfuron-methyl	1	0.997	39.9	11.4	58.3	3.3	0.999	83.3	6.5	90.0	1.0	0.996	24.8	36.3	63.5	3.5
101	Ethiofencarb	1	0.998	75.7	6.5	96.8	3.6	1.000	100.5	1.7	100.6	1.6	0.995	75.8	6.4	96.3	2.4
102	Ethion	1	0.995	73.3	12.4	101.4	4.6	0.996	89.8	9.4	102.1	5.6	0.994	87.0	5.0	96.7	4.2
103	Ethoprophos	1	0.998	70.3	9.6	99.4	4.9	0.995	73.1	16.9	92.0	7.3	0.999	96.1	10.0	99.7	4.0
104	Ethoxyquin	5	1.000	93.4	9.6	71.0	7.5	0.998	113.6	14.6	94.1	11.9	0.998	10.7	109.5	5.9	11.8
105	Ethoxysulfuron	1	0.994	37.0	16.1	55.9	7.2	0.990	26.5	53.8	79.3	8.0	0.990	6.7	170.9	71.9	5.8
106	Etofenprox	1	1.000	107.0	4.4	113.2	5.5	1.000	97.4	10.1	83.5	3.1	0.999	99.7	7.3	77.6	6.4

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
107	Etoxazole	1	0.999	106.2	3.3	112.5	3.6	0.996	80.9	7.4	90.2	5.1	1.000	90.2	6.3	82.6	6.8
108	Etrimfos	1	0.998	74.4	16.4	103.0	9.0	0.996	117.9	7.3	96.7	5.2	0.999	84.7	10.9	91.6	5.2
109	Famoxadone	5	0.998	106.6	28.9	100.7	23.8	0.979	96.5	20.1	93.1	7.1	0.985	87.0	21.4	102.5	10.0
110	Fenamidone	1	0.999	107.1	6.7	111.9	3.4	0.999	111.1	8.8	92.3	6.0	1.000	90.0	6.7	96.3	5.9
111	Fenamiphos	1	0.999	96.9	6.9	99.6	3.6	0.999	123.1	8.1	102.9	3.6	0.999	79.6	8.9	93.0	2.6
112	Fenarimol	1	0.999	118.9	15.2	109.8	8.2	0.993	81.2	10.3	94.1	5.6	0.995	96.7	18.0	97.7	4.9
113	Fenazaquin	1	1.000	87.2	5.1	93.3	4.5	1.000	103.1	1.8	101.1	3.3	1.000	89.3	2.7	92.3	2.2
114	Fenbuconazole	1	0.999	123.6	8.2	107.6	3.4	0.998	84.1	12.0	103.2	3.6	0.999	104.7	2.2	101.6	4.0
115	Fenhexamid	1	0.998	83.6	14.0	107.9	4.0	0.996	116.4	6.5	112.4	5.6	0.996	63.4	22.0	105.7	4.2
116	Fenobucarb (BPMC)	1	0.999	101.2	5.4	102.4	3.8	0.999	106.5	5.2	102.0	5.0	1.000	100.4	4.0	98.0	3.2
117	Fenothiocarb	1	0.992	71.4	9.2	102.7	3.2	0.996	80.2	6.4	98.4	4.2	0.995	74.6	5.0	99.4	1.9
118	Fenoxanil	1	0.998	85.2	8.0	106.3	2.3	0.998	108.8	5.3	103.4	7.6	0.997	83.6	6.1	103.8	5.3
119	Fenoxaprop-p-ethyl	1	0.996	88.0	8.6	101.7	6.6	0.999	95.9	6.8	103.0	3.7	0.999	87.4	7.5	96.8	2.9
120	Fenoxycarb	1	0.996	107.9	7.2	113.8	3.2	1.000	93.6	5.1	98.0	4.6	0.999	76.0	9.7	103.2	1.3
121	Fenpropathrin	5	1.000	77.6	17.3	107.6	10.6	1.000	119.0	7.4	105.5	2.8	0.997	125.2	12.4	95.6	3.6
122	Fenpyroximate	1	1.000	125.9	5.7	120.0	4.5	1.000	94.0	9.7	90.0	3.0	1.000	98.5	2.7	89.9	5.2
123	Fenthion	1	0.993	107.5	8.5	106.2	3.1	0.997	89.2	14.4	104.6	2.3	0.992	107.5	8.5	95.2	2.1
124	Ferimzone	1	0.999	81.5	9.8	75.0	4.6	0.999	90.5	4.8	60.3	9.0	0.999	85.7	6.8	67.6	7.2
125	Fipronil	1	1.000	99.1	7.5	95.5	6.0	1.000	89.2	8.0	98.0	2.2	1.000	101.3	5.8	101.0	2.7
126	Fluacrypyrim	1	0.992	101.7	12.2	101.5	5.6	0.998	101.3	11.9	108.5	5.1	0.995	77.7	15.9	108.7	3.9
127	Fluazinam	1	0.999	93.6	9.4	90.4	3.8	0.999	112.1	1.9	96.6	3.8	0.999	96.8	4.9	96.7	2.4
128	Flubendiamide	1	0.997	104.0	9.3	112.1	3.8	0.998	82.0	4.0	89.1	4.7	0.997	78.5	11.9	101.4	4.8
129	Flucetosulfuron	1	0.996	45.3	11.0	62.3	7.8	0.997	51.7	17.7	81.5	7.3	0.998	43.0	7.8	73.5	4.5
130	Fludioxonil	5	0.997	108.9	18.2	106.4	8.2	0.992	117.9	13.3	93.5	3.7	0.998	92.5	10.9	106.9	2.5
131	Flufenacet	1	0.996	70.6	15.1	114.5	4.3	0.999	107.3	5.0	103.8	4.2	0.991	70.4	9.9	101.0	3.2
132	Flufenoxuron	1	1.000	97.1	4.7	99.8	3.3	1.000	99.7	3.1	100.2	3.9	0.999	97.1	2.3	95.0	2.2
133	Flumiclorac-pentyl	1	0.998	103.5	11.3	101.7	5.5	0.997	83.8	9.3	101.7	1.4	0.999	88.7	6.8	95.2	3.2
134	Fluopicolide	1	0.995	96.0	12.2	104.3	4.8	1.000	112.6	13.7	99.5	3.2	0.989	62.8	16.8	97.0	5.8
135	Fluopyram	1	0.997	103.3	17.3	119.1	8.5	0.986	67.7	15.3	80.9	6.8	0.994	70.0	18.5	98.2	6.1
136	Fluquinconazole	1	0.991	115.3	18.5	108.4	3.6	0.995	132.5	14.3	98.6	9.0	0.993	96.3	13.1	107.1	5.1
137	Flusilazole	1	1.000	86.7	16.9	108.1	3.3	0.999	92.7	16.8	102.2	6.2	0.993	79.3	11.1	97.8	6.3
138	Flusulfamide	1	0.998	90.0	10.6	88.6	3.9	0.997	114.4	6.3	95.7	4.3	1.000	93.1	6.0	99.6	3.8
139	Flutolanil	1	0.993	91.3	8.1	106.2	4.6	1.000	115.4	4.4	95.1	2.9	0.993	72.1	5.4	98.6	3.6
140	Fluvalinate	1	1.000	102.3	6.2	100.0	4.1	1.000	105.0	2.4	93.1	2.6	1.000	99.6	7.5	90.2	3.6
141	Fluxapyroxad	1	0.993	8.7	265.1	120.0	11.3	1.000	133.8	17.7	85.7	8.8	0.993	66.8	19.9	95.4	10.9
142	Fonofos	1	0.999	96.5	13.2	97.9	5.4	1.000	103.4	8.1	96.0	3.2	0.999	99.6	4.7	102.1	4.3
143	Forchlorfenuron	1	0.999	94.4	6.5	101.0	3.3	0.999	90.4	5.5	97.8	2.9	1.000	92.2	3.2	97.2	2.4

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
144	Fosthiazate	1	0.997	92.5	6.5	103.2	5.0	0.999	99.7	7.7	92.7	6.3	0.999	97.8	7.2	96.7	3.6
145	Furathiocarb	1	1.000	98.0	7.0	101.5	5.6	0.995	74.1	8.5	93.2	7.0	1.000	87.6	7.4	94.5	4.2
146	Halfenprox	1	0.998	81.5	6.3	114.5	2.9	0.999	130.8	2.0	117.5	2.3	1.000	71.2	11.1	74.2	4.9
147	Halosulfuron-methyl	1	0.998	55.8	16.5	86.7	5.1	1.000	98.3	7.3	92.5	4.1	1.000	93.6	8.0	90.3	5.1
148	Haloxyfop	5	0.997	0.0	-	24.4	19.4	0.998	56.8	16.1	43.5	13.6	0.997	19.1	15.2	16.8	11.7
149	Haloxyfop-R-Methyl	1	0.992	100.1	3.4	103.7	3.2	0.996	80.1	7.6	103.6	1.9	0.999	82.2	8.4	95.5	3.4
150	Hexaconazole	1	0.998	118.9	11.4	101.8	4.1	1.000	88.2	6.8	94.9	3.2	0.999	96.8	7.6	97.2	3.3
151	Hexaflumuron	1	0.994	74.3	18.2	117.5	5.9	0.999	84.3	11.2	99.2	3.1	0.999	104.2	10.9	105.3	7.3
152	Hexazinone	1	0.997	80.0	6.2	96.2	3.5	1.000	91.0	4.5	93.6	7.0	0.999	87.6	5.7	96.3	2.8
153	Hexythiazox	1	1.000	88.5	4.4	96.8	3.7	1.000	95.7	4.3	100.2	3.9	1.000	93.0	2.2	94.2	1.0
154	Imazalil	1	1.000	115.0	5.0	98.9	4.3	1.000	100.5	8.0	93.9	4.0	1.000	88.6	7.3	87.8	4.1
155	Imazamox	10	0.999	17.7	155.4	18.3	11.4	0.999	35.8	12.2	34.2	13.4	0.999	0.5	400.7	8.9	10.8
156	Imazapic	1	0.996	-	-	8.8	18.1	0.995	32.2	16.0	38.6	12.9	0.999	-	-	9.5	11.0
157	Imazaquin	1	0.994	-	-	5.8	13.2	1.000	26.8	18.8	37.9	9.2	0.999	-	-	4.0	33.8
158	Imazethapyr	1	0.994	-	-	14.6	26.3	0.999	49.1	14.0	45.0	17.8	1.000	-	-	12.4	19.2
159	Imazosulfuron	1	0.994	0.3	3773.8	57.9	7.6	0.970	39.2	33.1	74.7	9.0	0.993	-	-	58.3	9.6
160	Imibenconazole	1	0.999	94.7	11.9	107.3	2.7	0.999	91.0	5.4	100.5	3.3	0.999	83.9	5.7	98.3	3.6
161	Imicyafos	1	0.998	102.0	5.8	115.6	4.8	0.999	101.9	7.1	88.9	6.1	1.000	101.2	8.6	98.4	3.9
162	Imidacloprid	1	0.994	96.3	10.7	101.4	4.1	0.990	98.8	11.8	97.7	13.3	0.999	95.8	6.9	97.5	1.8
163	Inabenfide	20	0.951	98.8	37.9	89.9	18.5	0.989	126.3	11.1	75.9	18.7	0.996	82.5	31.6	102.0	13.1
164	Indoxacarb	1	0.996	91.9	15.9	106.3	5.1	1.000	101.3	8.7	102.0	5.1	0.993	69.4	20.2	110.4	4.2
165	Iprobenfos	1	0.999	92.9	10.7	99.0	3.0	0.998	86.8	9.5	101.2	3.6	0.999	97.6	5.5	96.2	5.5
166	Iprovalicarb	1	0.999	79.9	5.4	103.7	4.0	1.000	86.0	4.1	92.0	5.1	0.998	76.6	2.8	99.6	1.6
167	Isazofos	1	0.994	85.6	6.4	109.6	2.6	0.999	97.1	9.3	100.1	1.2	0.996	76.1	3.0	101.0	3.0
168	Isoprocarb	1	0.999	99.2	4.1	103.5	2.4	1.000	99.4	5.0	99.8	2.8	0.999	94.4	5.0	102.8	2.4
169	Isoprothiolane	1	0.991	79.3	3.2	104.3	2.9	0.995	95.1	15.0	107.5	8.1	0.994	74.3	2.3	104.8	2.3
170	Isoproturon	1	0.997	91.7	7.7	101.4	3.3	0.999	94.7	4.1	95.0	2.1	0.999	84.3	6.9	99.2	1.8
171	Isopyrazam	1	0.999	101.6	7.2	107.1	5.4	1.000	94.7	7.9	98.8	5.6	0.996	72.9	6.5	97.2	4.7
172	Isoxathion	1	0.997	76.2	10.6	99.0	3.2	0.995	75.8	4.9	104.7	3.4	0.998	82.6	6.7	101.4	1.7
173	Kresoxim-methyl	1	0.991	101.9	17.2	106.3	4.7	0.990	95.2	5.7	101.6	4.2	0.992	64.8	24.8	108.4	7.1
174	Lactofen	1	0.999	106.9	7.5	110.0	3.0	0.998	91.1	6.1	105.6	4.0	1.000	89.8	3.2	102.8	2.5
175	Lepimectin A3	1	0.995	-	-	71.9	3.8	0.999	114.7	9.9	104.1	3.3	0.998	125.5	14.1	82.0	7.3
176	Lepimectin A4	1	0.996	-	-	83.6	5.9	1.000	124.9	6.4	114.7	3.2	1.000	77.6	47.2	71.9	6.1
177	Linuron	1	0.999	88.0	16.7	105.9	7.9	0.999	107.7	10.1	95.4	6.5	0.999	87.9	9.8	100.5	6.1
178	Lufenuron	2	0.996	81.8	19.3	108.8	5.5	1.000	114.3	16.6	92.2	8.1	1.000	92.8	16.4	100.8	8.1
179	Malathion	1	0.995	86.2	12.9	108.2	2.9	0.989	75.3	8.9	102.4	6.5	0.999	87.4	4.7	104.9	2.2
180	Mandipropamid	1	0.996	106.2	4.9	109.9	2.2	0.999	99.8	5.6	95.8	3.5	0.996	78.7	4.0	102.0	3.1

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
181	Mecarbam	1	0.996	82.0	8.5	114.6	1.5	0.997	94.4	3.7	99.6	4.6	0.999	90.2	8.9	106.4	4.5
182	Mecoprop-P	5	0.996	-	-	8.4	31.1	0.998	50.6	22.8	40.2	11.1	1.000	30.3	51.0	17.2	12.4
183	Mefenacet	1	0.995	84.2	4.4	107.4	3.3	0.996	100.6	13.2	90.4	6.0	0.998	83.2	6.1	101.3	3.8
184	Mefenpyr-diethyl	1	0.998	94.8	9.6	105.4	4.2	0.999	91.5	5.6	99.5	2.3	1.000	95.5	5.5	102.2	2.6
185	Mepanipyrim	1	0.994	94.8	10.4	93.0	5.5	1.000	109.4	6.2	90.3	4.5	0.995	84.2	14.0	96.5	5.7
186	Metalaxyl	1	1.000	106.7	5.0	109.6	5.5	0.998	90.7	8.7	91.4	6.5	0.997	80.8	10.3	106.8	4.5
187	Metamifop	1	1.000	101.1	2.7	102.7	4.0	1.000	100.4	4.2	106.3	3.1	1.000	93.9	6.1	97.9	3.5
188	Metazosulfuron	1	0.999	69.4	14.2	69.7	12.0	1.000	94.7	10.0	83.7	5.9	0.999	73.9	10.1	81.5	5.3
189	Metconazole	1	0.999	101.8	5.5	107.1	3.8	1.000	97.5	2.6	98.6	1.4	0.999	89.9	2.8	98.5	3.2
190	Methabenzthiazuron	1	0.999	109.3	4.9	109.2	5.3	0.999	101.2	6.2	87.3	6.4	0.998	77.1	11.5	100.0	3.6
191	Methamidophos	1	1.000	75.3	4.2	84.0	4.3	1.000	55.5	19.9	73.5	5.6	0.999	70.4	7.0	76.6	4.0
192	Methidathion	1	0.994	78.2	20.7	114.6	7.8	0.997	86.7	18.5	95.3	5.9	0.995	101.9	15.4	102.4	4.8
193	Methiocarb	1	0.994	95.6	5.0	112.9	2.3	1.000	113.6	5.5	97.0	2.6	0.999	76.5	8.1	101.6	4.8
194	Methomyl	1	0.995	193.6	7.7	219.3	2.4	0.999	90.3	19.8	111.2	10.5	0.995	91.3	10.3	125.9	3.1
195	Methoxyfenozide	1	0.990	63.6	29.4	101.6	8.5	0.946	47.7	143.4	88.4	18.7	0.998	94.0	16.0	101.1	2.8
196	Metobromuron	1	0.995	77.5	15.3	93.3	5.5	0.995	88.6	8.5	97.4	3.7	0.998	72.8	12.2	101.2	4.5
197	Metolachlor	1	0.999	106.4	4.1	108.7	2.4	0.991	107.3	7.2	92.4	7.8	0.999	91.9	10.8	93.9	7.2
198	Metolcarb	1	0.996	91.1	6.5	100.8	3.2	0.999	95.0	4.9	97.0	4.4	1.000	92.5	2.8	103.1	2.9
199	Metominostrobin	1	0.997	73.0	6.5	100.8	4.4	1.000	99.7	5.7	98.8	3.1	0.998	90.3	5.3	103.0	3.3
200	Metrafenone	1	0.994	88.4	12.2	102.1	3.0	0.999	86.9	4.5	103.2	3.3	0.998	69.5	6.8	100.7	1.8
201	Metribuzin	1	0.996	92.1	10.2	120.0	1.5	0.999	88.9	13.7	94.2	6.4	0.999	88.0	6.5	107.6	2.9
202	Mevinphos	1	1.000	89.9	6.7	102.4	5.6	0.998	76.6	12.1	100.6	15.6	0.999	104.9	3.6	94.0	4.3
203	Milbemectin A3	1	0.995	450.7	42.5	155.3	4.8	0.998	111.9	10.0	91.7	2.2	0.999	116.9	22.2	92.5	5.0
204	Milbemectin A4	1	1.000	73.1	55.0	96.9	6.5	0.999	99.8	7.0	93.4	3.2	0.997	-	-	76.2	5.7
205	Molinate	1	0.999	97.8	6.6	103.4	3.6	0.999	91.7	8.1	103.0	5.2	0.998	88.9	3.6	99.1	2.1
206	Monocrotophos	1	0.998	80.7	6.9	89.9	3.5	0.999	84.1	9.8	92.1	7.8	1.000	79.2	10.6	89.2	3.2
207	Myclobutanil	1	0.996	93.1	12.9	111.5	2.9	0.996	95.4	12.3	104.0	3.1	0.998	88.9	8.0	106.7	1.9
208	Napropamide	1	0.997	79.1	13.7	94.9	8.7	1.000	100.8	6.2	93.6	3.2	0.999	93.3	8.5	98.3	3.6
209	Nicosulfuron	1	0.999	13.6	17.5	27.5	4.5	0.999	33.9	17.3	48.9	10.5	0.999	7.8	76.3	35.6	8.1
210	Novaluron	1	0.999	116.9	3.4	106.2	2.5	0.999	92.3	5.9	96.1	4.0	1.000	92.3	2.5	96.9	4.2
211	Nuarimol	2	0.999	100.1	6.7	104.0	3.7	0.999	115.8	5.3	97.4	4.0	1.000	86.2	8.1	101.7	4.5
212	Ofurace	1	0.996	87.5	4.3	99.6	4.0	0.999	92.1	8.5	99.9	4.6	0.999	82.5	7.7	100.8	2.3
213	Omethoate	1	0.994	73.3	8.3	80.1	4.6	0.998	80.7	13.0	74.0	14.9	0.996	76.1	6.4	89.3	7.8
214	Orysastrobin	1	1.000	106.1	2.3	104.6	4.8	1.000	98.0	7.9	104.3	5.5	1.000	100.8	3.1	99.1	2.4
215	Oxadiazon	1	0.999	107.9	19.9	101.6	8.6	0.999	111.8	10.6	108.2	4.4	0.998	80.2	5.8	99.8	7.3
216	Oxadixyl	1	0.999	81.5	4.5	102.7	3.5	0.999	88.1	9.3	97.0	4.9	1.000	89.0	6.7	99.0	1.7
217	Oxamyl	1	0.997	82.4	6.0	99.7	2.8	0.999	82.4	6.5	93.0	8.7	1.000	83.5	3.5	98.7	2.0

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
218	Oxaziclomefone	5	0.999	90.2	6.9	107.8	3.6	0.999	96.2	2.2	103.4	2.2	1.000	98.3	4.7	99.4	3.3
219	Oxydemeton-methyl	1	0.997	81.8	5.6	93.2	3.3	1.000	70.8	8.7	81.5	7.9	1.000	84.1	4.4	87.9	2.1
220	Paclobutrazol	2	0.999	97.9	8.0	112.3	5.4	1.000	96.9	7.0	100.9	3.5	0.998	83.7	6.3	102.5	3.8
221	Pebulate	1	0.998	92.8	12.1	105.0	8.7	0.997	94.8	7.7	101.7	6.5	0.999	84.3	17.7	100.5	6.2
222	Penconazole	1	0.998	112.2	8.7	110.7	4.2	1.000	98.9	5.1	100.2	3.3	0.999	82.7	5.8	100.9	4.5
223	Pencycuron	1	0.999	128.9	15.1	126.2	8.0	0.985	95.3	7.9	86.1	13.6	0.998	82.9	8.6	97.8	8.0
224	Pendimethalin	1	1.000	99.4	5.0	103.7	3.5	1.000	100.6	4.1	99.3	2.5	1.000	98.2	2.4	95.8	2.8
225	Penoxsulam	1	0.996	32.8	12.2	66.3	4.8	0.998	79.4	7.7	93.8	4.8	0.995	38.8	18.1	79.2	3.6
226	Penthiopyrad	5	0.990	86.3	5.1	109.7	4.4	0.993	75.3	4.7	105.4	3.1	0.997	72.3	7.8	110.1	3.5
227	Phenmedipham	1	0.997	92.9	6.2	110.4	3.3	1.000	89.4	6.7	100.7	3.3	0.999	91.0	5.7	98.6	4.5
228	Phenothrin	1	1.000	84.6	6.9	94.6	4.6	0.999	105.2	3.4	100.0	2.1	1.000	82.4	6.6	83.3	2.9
229	Phenthoate	1	0.995	111.9	10.7	109.1	2.2	0.999	89.0	6.0	106.6	2.1	0.993	86.7	5.1	105.1	3.1
230	Phorate	2	0.998	94.5	18.0	108.8	9.8	1.000	89.8	15.7	101.3	5.4	0.999	107.4	10.8	103.8	7.5
231	Phosalone	1	0.992	91.4	11.2	110.0	4.9	0.998	90.3	9.3	107.1	3.4	0.991	66.3	9.5	104.5	2.8
232	Phosmet	5	0.996	81.2	6.3	109.9	4.0	1.000	111.9	9.5	101.2	4.2	0.997	92.4	5.7	105.0	1.8
233	Phosphamidon	1	1.000	97.7	7.2	101.7	3.8	1.000	92.2	3.4	98.2	4.9	1.000	102.6	2.1	103.0	2.2
234	Phoxim	1	0.999	97.7	8.3	115.9	2.9	0.998	76.6	15.3	109.2	7.7	0.998	90.1	5.7	96.7	5.1
235	Picolinafen	1	0.994	87.1	6.1	103.1	3.7	0.994	77.9	3.0	106.3	2.0	0.998	85.4	1.6	102.1	2.0
236	Picoxystrobin	1	0.996	102.6	7.5	102.3	4.2	0.999	95.8	5.2	99.0	2.2	0.999	94.9	4.9	105.9	3.5
237	Piperophos	5	0.999	96.1	6.0	102.7	3.8	1.000	93.5	8.2	94.4	2.4	0.998	78.3	8.1	94.8	4.1
238	Pirimicarb	1	0.999	96.8	4.4	97.9	3.1	1.000	88.9	5.8	95.3	4.6	1.000	91.8	4.0	98.0	1.6
239	Pirimiphos-ethyl	1	0.999	104.3	4.7	91.7	2.5	1.000	99.8	5.2	105.0	3.3	1.000	95.4	3.6	92.7	2.2
240	Pirimiphos-methyl	1	0.998	117.6	4.8	102.5	6.0	1.000	102.4	7.0	99.0	4.1	0.998	83.3	6.7	100.0	2.7
241	Pretilachlor	1	0.999	94.7	3.0	105.2	2.6	1.000	100.2	2.6	98.8	2.9	1.000	89.6	2.7	97.4	1.8
242	Probenazole	1	0.993	60.3	12.5	78.8	4.4	0.994	85.2	5.5	92.1	3.9	0.997	38.6	22.1	78.3	4.8
243	Prochloraz	1	1.000	112.3	8.8	107.8	4.4	0.999	100.2	6.7	99.0	2.7	1.000	90.2	6.0	97.4	2.2
244	Profenofos	1	1.000	108.7	5.4	111.6	2.7	0.999	91.6	4.9	105.2	1.4	0.999	89.8	6.9	100.1	4.0
245	Promecarb	1	0.996	89.2	5.8	109.0	3.1	0.998	99.7	11.1	101.2	4.7	0.999	81.9	4.2	103.6	4.0
246	Prometryn	1	0.996	101.3	5.1	89.6	4.1	0.999	108.5	12.0	103.6	4.6	0.994	89.7	9.9	95.1	7.7
247	Propachlor	1	0.995	81.6	7.1	99.9	4.1	0.998	79.7	7.7	100.1	3.4	0.995	81.0	9.4	106.4	3.4
248	Propamocarb	1	0.991	77.5	8.2	65.1	10.1	0.999	64.5	4.7	67.6	9.1	0.999	72.4	9.3	77.7	7.6
249	Propanil	5	1.000	93.7	15.3	92.0	7.1	0.995	116.1	11.3	101.6	2.9	1.000	108.8	9.0	102.2	2.9
250	Propaquizafop	1	0.996	84.8	8.5	103.8	3.9	0.993	78.7	10.4	100.5	2.7	0.997	78.3	8.0	99.1	5.0
251	Propazine	1	0.999	83.9	17.6	104.4	6.1	1.000	102.8	8.5	95.8	1.5	0.999	84.8	6.4	97.1	3.3
252	Propiconazole	1	0.999	106.3	6.5	115.8	2.4	1.000	97.9	7.6	97.3	4.5	0.999	83.8	11.6	99.2	4.4
253	Propisochlor	1	0.999	75.8	21.0	100.1	7.6	0.996	100.9	12.3	106.7	9.7	1.000	84.3	24.0	103.0	6.0
254	Propoxur	1	0.998	94.1	2.8	107.1	3.5	1.000	95.0	4.7	98.3	3.0	0.999	81.5	4.3	102.1	1.7

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
255	Propyzamide	1	0.985	85.2	11.5	107.8	7.6	0.988	115.2	13.5	107.3	8.0	0.994	72.7	9.2	106.4	4.7
256	Prothiofos	1	0.996	94.2	5.1	103.7	3.2	1.000	103.6	3.5	92.9	3.4	1.000	95.5	4.7	88.4	2.8
257	Pymetrozine	2	0.998	70.1	18.0	91.2	2.6	0.986	96.2	11.7	100.6	5.4	0.996	74.0	18.9	101.5	7.2
258	Pyraclofos	1	0.996	81.3	17.6	117.6	4.6	0.991	71.5	17.8	97.9	10.7	0.993	73.2	8.5	100.0	6.9
259	Pyraclostrobin	5	0.998	106.4	3.9	100.5	1.7	1.000	92.4	3.8	99.5	3.0	0.998	81.9	4.9	99.6	3.1
260	Pyrazolynate	1	0.996	104.9	7.5	100.7	5.0	0.999	94.1	9.8	97.7	3.3	0.996	81.9	2.9	88.4	3.1
261	Pyrazophos	1	0.991	123.7	8.1	109.3	5.0	0.997	106.2	14.6	96.1	12.2	0.998	95.9	26.8	102.1	9.1
262	Pyrazoxyfen	1	0.998	90.3	7.8	113.2	2.5	1.000	104.4	4.6	96.9	3.7	0.998	79.4	8.9	98.5	2.8
263	Pyribenzoxim	1	0.995	71.5	10.3	78.7	7.4	0.994	115.8	4.2	87.4	5.5	0.989	137.1	6.0	94.0	6.7
264	Pyributicarb	1	0.999	96.6	5.9	101.0	3.5	0.993	84.2	8.9	103.6	2.5	0.999	89.5	3.2	94.1	1.7
265	Pyridaben	1	0.998	86.8	5.3	111.4	5.9	1.000	96.7	6.2	98.3	3.8	1.000	89.6	5.2	93.1	3.5
266	Pyridaphenthion	1	0.990	89.2	13.6	109.1	10.4	0.997	106.8	8.5	88.2	16.3	0.986	47.0	28.9	114.6	13.8
267	Pyridate	1	1.000	65.8	10.1	75.9	3.1	0.943	175.1	7.9	77.2	30.0	0.964	111.2	5.0	50.5	7.1
268	Pyrifluquinazon	1	0.997	87.1	9.9	109.9	2.6	1.000	116.4	8.3	100.3	4.7	0.999	78.8	5.6	97.6	3.8
269	Pyrimethanil	5	0.995	126.5	5.9	100.6	10.6	1.000	92.6	7.8	90.4	6.5	0.999	101.7	18.1	102.7	8.1
270	Pyrimidifen	1	0.998	80.1	16.8	103.1	9.4	0.999	73.7	9.7	92.7	6.1	1.000	90.4	8.7	95.1	5.9
271	Pyriminobac-methyl E	1	1.000	107.9	3.8	104.6	6.8	1.000	102.5	7.1	98.1	5.3	0.999	98.0	7.0	96.4	3.7
272	Pyriminobac-methyl Z	1	1.000	106.6	6.1	97.3	5.6	0.999	90.0	11.5	98.4	3.8	0.998	87.6	6.0	99.3	3.7
273	Pyrimisulfan	1	0.996	100.1	17.4	104.5	7.2	0.992	84.6	15.0	84.2	14.5	0.998	93.9	8.6	94.4	7.5
274	Pyriproxyfen	1	0.998	107.7	2.4	108.4	3.1	0.998	87.6	5.7	102.7	4.7	0.999	90.6	4.7	92.8	3.5
275	Pyroquilon	1	0.997	87.1	5.2	109.8	2.2	0.999	86.4	5.0	95.7	3.8	0.998	79.2	8.7	101.3	3.8
276	Quinoclamine	1	0.996	93.9	10.6	119.1	6.1	0.999	89.2	6.1	91.2	6.1	0.995	87.8	16.0	106.9	7.6
277	Rimsulfuron	1	0.995	54.9	21.3	59.0	6.4	0.997	42.3	24.2	67.5	6.3	0.998	37.0	19.4	61.4	7.6
278	Saflufenacil	1	1.000	96.8	15.1	79.5	7.8	0.998	88.6	19.7	89.4	5.5	0.999	75.2	11.2	83.1	3.8
279	Sethoxydim	1	0.999	100.2	13.2	111.0	8.9	0.993	71.2	14.5	93.5	4.9	0.987	76.1	11.9	87.9	3.1
280	Simazine	1	0.997	79.5	7.9	108.2	5.0	1.000	84.5	15.0	101.1	7.8	0.997	90.8	8.8	107.5	4.6
281	Simeconazole	1	0.996	110.1	11.0	112.2	6.1	0.996	87.0	7.0	95.9	2.7	1.000	93.2	3.7	104.4	4.7
282	Simetryn	1	1.000	103.2	4.6	101.7	3.7	0.999	88.0	3.2	88.3	3.8	1.000	94.0	5.2	95.3	3.5
283	Spinetoram (XDE-175-J)	1	0.999	107.4	7.7	93.7	5.1	1.000	104.8	6.6	93.4	2.3	0.999	88.3	2.8	98.1	4.0
284	Spinetoram (XDE-175-L)	1	0.999	103.9	6.0	87.8	4.6	1.000	111.2	10.7	97.5	2.1	1.000	84.1	7.0	88.7	7.6
285	Spinosyn A	1	1.000	100.4	7.4	115.5	3.9	0.999	96.7	5.3	78.9	7.3	1.000	100.8	6.2	93.7	2.9
286	Spinosyn D	1	0.999	112.7	9.6	105.8	3.7	0.999	86.7	5.6	95.3	5.9	1.000	96.7	6.3	99.5	3.9
287	Spirotetramat	1	0.993	92.2	15.3	97.0	6.4	0.996	116.0	15.1	86.2	9.8	0.994	92.3	13.3	90.6	6.4
288	Sulfoxaflor	1	0.996	91.9	19.7	110.7	12.7	0.998	72.0	18.7	102.1	6.1	1.000	110.8	19.2	103.9	4.6
289	Sulprofos	1	0.999	94.7	10.5	105.7	4.3	1.000	102.8	6.3	96.4	5.6	0.999	102.5	3.3	86.8	3.2
290	TCMTB	1	0.998	80.2	10.7	76.0	5.5	1.000	91.8	5.6	94.2	3.8	1.000	88.4	6.5	91.5	3.9
291	Tebuconazole	1	0.998	96.7	6.3	109.2	5.0	0.999	90.6	8.0	102.5	2.5	0.999	85.6	7.3	101.8	3.2

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
292	Tebufenozide	1	0.998	134.8	18.4	112.2	7.5	0.980	66.8	19.8	102.5	9.4	0.997	71.5	19.9	93.5	11.2
293	Tebufenpyrad	1	0.998	85.4	6.5	100.0	4.2	0.999	99.8	7.1	103.1	4.7	0.999	72.9	10.3	93.3	3.0
294	Tebupirimfos	1	0.999	92.5	8.6	101.0	7.7	1.000	96.8	5.5	102.6	4.3	1.000	88.3	5.5	95.0	2.6
295	Teflubenzuron	2	0.999	116.8	15.5	107.4	8.7	0.996	92.7	10.8	96.7	2.3	0.995	89.3	18.3	103.4	5.9
296	Terbuthylazine	1	0.995	73.8	10.8	101.0	1.7	0.999	118.5	7.7	97.2	4.9	0.998	90.9	8.2	95.9	2.8
297	Terbutryn	1	0.999	87.1	15.0	93.2	6.5	0.995	81.1	14.5	99.2	12.5	0.999	100.4	9.6	96.3	2.3
298	Tetrachlorvinphos	1	1.000	90.0	9.9	112.3	5.1	0.999	84.3	6.2	101.4	4.6	0.997	76.9	10.6	104.4	1.5
299	Tetraconazole	1	0.999	92.4	7.4	111.5	4.0	1.000	95.4	8.1	101.9	4.8	0.995	89.3	7.9	104.1	1.8
300	Thenylchlor	1	0.991	110.8	9.8	104.9	7.0	1.000	99.8	7.8	103.0	4.3	1.000	78.3	9.9	103.0	5.0
301	Thiabendazole	1	0.996	88.0	7.1	102.8	5.6	1.000	80.0	6.5	71.2	3.9	0.997	108.3	6.0	89.6	2.5
302	Thiacloprid	1	0.991	88.9	5.2	101.5	4.6	0.996	76.6	7.0	95.2	6.8	1.000	97.8	5.1	100.6	3.1
303	Thiamethoxam	1	0.990	84.4	7.6	103.9	3.0	0.998	79.3	10.5	98.3	8.2	0.998	77.8	7.7	98.0	1.7
304	Thiazopyr	1	0.991	88.8	19.5	104.9	5.8	0.999	82.4	10.2	98.4	2.8	0.991	95.7	17.9	112.8	5.2
305	Thidiazuron	1	0.999	84.5	8.1	101.1	3.4	0.999	86.2	4.9	92.1	6.9	0.997	74.1	5.3	96.6	4.0
306	Thifensulfuron-methyl	1	0.999	49.6	8.8	55.7	4.4	1.000	68.6	3.5	81.5	4.2	0.999	50.4	11.2	68.5	2.6
307	Thifluzamide	1	0.998	114.1	12.7	102.0	5.3	1.000	72.9	13.6	96.2	6.2	0.998	104.3	13.9	102.3	6.0
308	Thiobencarb	1	0.994	101.7	7.2	100.8	3.1	0.999	92.4	3.8	103.8	3.0	0.999	82.5	6.1	103.1	3.4
309	Thiodicarb	1	0.993	-	-	-	-	0.995	104.7	2.6	91.1	3.1	0.998	79.7	7.0	82.8	2.9
310	Thiophanate-methyl	1	0.992	94.5	6.2	131.3	2.3	0.991	117.3	3.7	109.4	3.9	0.992	105.6	4.6	102.0	1.9
311	Tiadinil	2	0.998	152.9	17.8	107.8	3.4	0.985	91.9	21.2	100.6	13.5	0.988	78.1	14.2	97.8	5.2
312	Tolclofos-methyl	2	0.991	85.7	25.8	87.6	16.7	0.998	114.4	19.1	106.2	6.4	0.999	108.6	9.3	99.5	8.6
313	Tolfenpyrad	1	0.998	88.2	8.6	98.9	2.9	0.994	62.8	15.7	98.0	3.1	0.997	67.3	10.5	97.6	4.9
314	Triadimefon	1	0.998	84.9	11.5	110.1	2.6	0.999	117.5	18.9	98.3	10.3	0.995	78.7	7.0	108.7	3.0
315	Triadimenol	2	0.991	80.2	15.6	104.4	6.1	0.997	92.2	15.4	103.3	8.0	0.998	75.7	19.5	106.0	4.9
316	Tri-allate	5	0.999	101.6	12.3	99.0	4.7	0.998	99.7	9.5	104.1	3.7	1.000	91.6	8.7	93.8	4.5
317	Triazophos	2	0.998	119.8	8.9	116.3	4.1	0.998	100.7	13.5	96.2	5.9	0.995	81.8	8.1	106.5	8.6
318	Tribenuron-methyl	5	0.995	66.0	6.2	58.5	2.2	0.999	62.9	5.9	61.5	3.3	0.999	58.6	3.5	62.4	3.6
319	Tribufos	1	1.000	90.1	2.9	95.3	3.1	1.000	102.0	2.5	108.7	1.9	1.000	89.4	3.7	88.3	2.3
320	Trichlorfon	1	0.997	79.6	16.3	103.5	4.4	0.999	102.7	14.0	98.2	8.7	0.998	101.4	7.2	105.5	6.0
321	Triclopyr	5	0.999	113.9	8.0	101.3	4.5	0.987	0.0	-	101.8	19.3	0.996	85.5	10.8	98.1	3.7
322	Tricyclazole	1	0.999	103.0	4.4	102.2	2.4	0.999	70.0	12.9	78.7	8.8	1.000	90.1	7.7	90.8	4.3
323	Trifloxystrobin	1	0.999	90.3	7.2	114.7	3.6	1.000	109.4	8.4	92.5	4.5	0.996	84.5	9.0	95.6	7.5
324	Triflumizole	1	0.998	103.0	6.7	102.9	2.5	0.999	90.1	6.9	99.6	2.6	1.000	90.6	6.7	93.7	3.4
325	Triflumuron	1	0.996	84.2	5.2	110.9	6.1	1.000	88.7	4.0	99.7	4.0	0.997	76.0	9.5	104.6	4.7
326	Trimethacarb	1	0.996	82.4	5.8	106.0	3.4	0.997	86.7	6.6	100.5	4.1	0.998	84.6	7.0	102.8	3.3
327	Triticonazole	1	0.998	94.9	7.9	102.1	1.9	1.000	97.8	6.9	94.1	1.3	0.999	88.1	6.3	102.3	2.1
328	Uniconazole	1	0.993	119.7	2.7	106.6	6.9	0.994	84.3	18.5	104.6	9.2	0.993	90.1	3.4	102.5	5.7

No.	Name	LOQ	Brown rice					Orange					Spinach				
			r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %	r^2	10 (ng/g) Rec.,%	RSD, %	50 (ng/g) Rec.,%	RSD, %
329	Vamidothion	1	0.999	93.2	4.9	99.4	2.6	0.999	92.6	7.0	93.3	14.0	1.000	92.7	3.7	98.1	3.7
330	Vernolate	1	0.997	76.9	17.9	97.4	11.5	0.998	79.1	18.6	99.9	6.0	0.999	103.5	12.3	98.6	6.2
331	XMC	1	0.998	99.4	3.9	101.9	3.6	1.000	105.4	5.0	96.4	2.8	0.999	89.6	4.8	101.9	2.7
332	Zoxamide	1	0.996	100.2	12.0	110.2	2.7	0.999	98.0	4.3	101.7	3.0	0.999	70.2	5.8	100.1	3.2

References

Alder L, Greulich K, Kempe G, Vieth B. (2006) Residue analysis of 500 high priority pesticides: Better by GC–MS or LC–MS/MS?. *Mass Spectrom Rev*. 25:838-865.

Almeida C, Serodio P, Florencio MH, Nogueira JM. (2007) New strategies to screen for endocrine-disrupting chemicals in the Portuguese marine environment utilizing large volume injection-capillary gas chromatography-mass spectrometry combined with retention time locking libraries (LVI-GC-MS-RTL). *Anal Bioanal Chem*. 387:2569-2583.

Anastassiades M, EURL. (2006). The QuEChERS Method–Background Information and Recent Developments. http://www.eurl-pesticides.eu/library/docs/srm/1stws2006_lecture_anastassiades_quechers.pdf

Anastassiades M, Kolberg DI, Benkenstein A, Eichhorn E, Zechmann S, Mack D, et al. (2016) Quick method for the analysis of numerous highly polar pesticides in foods of plant origin via LC-MS/MS involving simultaneous extraction with methanol (QuPPe-Method). EU Reference Laboratories (EURL-SRM).

Anastassiades M, Lehotay SJ, Štajnbaher D, Schenck FJ. (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *J AOAC Int*. 86:412-431.

Anastassiades M, Maštovská K, Lehotay SJ. (2003) Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides. *J Chromatogr A*. 1015:163-184.

Andrade GCRM, Monteiro SH, Francisco JG, Figueiredo LA, Botelho RG, Tornisielo VL. (2015) Liquid chromatography–electrospray ionization tandem mass spectrometry and dynamic multiple reaction monitoring method for determining multiple pesticide residues in tomato. *Food Chem*. 175:57-65.

Aysal P, Ambrus Á, Lehotay SJ, Cannavan A. (2007) Validation of an efficient method for the determination of pesticide residues in fruits and vegetables using ethyl acetate for extraction. *J Environ Sci Health, Part B*. 42:481-490.

Aznar R, Albero B, Sánchez-Brunete C, Miguel E, Martín-Girela I, Tadeo JL. (2016) Simultaneous determination of multiclass emerging contaminants in aquatic plants by ultrasound-assisted matrix solid-phase dispersion and GC-MS. *Environ Sci Pollut Res*. 23:1-10.

Banerjee K, Utture S. (2015) Recent developments in gas chromatography–mass spectrometry. In: *Mass spectrometry for the analysis of pesticide residues and their metabolites*. Hoboken, NJ: John Wiley & Sons, Inc. p. 91-112.

Belmonte Valles N, Retamal M, Martinez-Uroz MA, Mezcua M, Fernandez-Alba AR, de Kok A. (2012) Determination of chlorothalonil in difficult-to-analyse vegetable matrices using various multiresidue methods. *Analyst*. 137:2513-2520.

Blumberg LM, Klee MS. (1998) Method translation and retention time locking in partition GC. *Anal Chem*. 70:3828-3839.

Bordin AB, Minetto L, do Nascimento Filho I, Beal LL, Moura S. (2017) Determination of Pesticide Residues in Whole Wheat Flour Using Modified QuEChERS and LC–MS/MS. *Food Anal Methods*. 10:1-9.

Bratinova S, Raffael B, Simoneau C. (2009) Guidelines for performance criteria and validation procedures of analytical methods used in controls of food contact materials. *EUR 24105 EN - 1st edition*.

Bresin B, Piol M, Fabbro D, Mancini MA, Casetta B, Del Bianco C. (2015) Analysis of organo-chlorine pesticides residue in raw coffee with a modified “quick easy cheap effective rugged and safe” extraction/clean up procedure for reducing the impact of caffeine on the gas chromatography–mass spectrometry measurement. *J Chromatogr A*. 1376:167-171.

Bruins AP. (1998) Mechanistic aspects of electrospray ionization. *J Chromatogr A*. 794:345-357.

Buchenauer H, Edgington LV, Grossmann F. (1973) Photochemical transformation of thiophanate-methyl and thiophanate to alkyl benzimidazol-2-yl carbamates. *Pesticide Science*. 4:343-348.

Caldas SS, Gonçalves FF, Primel EG, Prestes OD, Martins ML, Zanella R. (2011) Principais técnicas de preparo de amostra para a determinação de resíduos de agrotóxicos em água por cromatografia líquida com detecção por arranjo de diodos e por espectrometria de massas. *Química Nova*. 34:1604-1617.

Chamkasem N, Harmon T. (2016) Direct determination of glyphosate, glufosinate, and AMPA in soybean and corn by liquid chromatography/tandem mass spectrometry. *Anal Bioanal Chem*. 408:4995-5004.

Chamkasem N, Ollis LW, Harmon T, Lee S, Mercer G. (2013) Analysis of 136 pesticides in avocado using a modified QuEChERS method with LC-MS/MS and GC-MS/MS. *J Agric Food Chem*. 61:2315-2329.

Charalampous Ac, Miliadis GE, Koupparis MA. (2015) A new multiresidue method for the determination of multiclass pesticides, degradation products and PCBs in water using LC–MS/MS and GC–MS(n) systems. *International Journal of Environmental Analytical Chemistry*. 95:1283-1298.

Chen M-X, Cao Z-Y, Jiang Y, Zhu Z-W. (2013) Direct determination of glyphosate and its major metabolite, aminomethylphosphonic acid, in fruits and vegetables by mixed-mode hydrophilic interaction/weak anion-exchange liquid chromatography coupled with electrospray tandem mass spectrometry. *J Chromatogr A*. 1272:90-99.

Chen Y, Lopez S, Hayward DG, Park HY, Wong JW, Kim SS, et al. (2016) Determination of multiresidue pesticides in botanical dietary supplements using gas chromatography–triple-quadrupole mass spectrometry (GC-MS/MS). *J Agric Food Chem*. 64:6125-6132.

Cho J, Lee J, Lim C-U, Ahn J. (2016) Quantification of pesticides in food crops using QuEChERS approaches and GC-MS/MS. *Food Addit Contam, Part A*. 33:1803-1816.

Choi H, Moon JK, Seo JS, Kim JH. (2013) Establishment of retention index library on gas chromatography-mass spectrometry for nontargeted metabolite profiling approach. *J Korean Soc Appl Biol Chem*. 56:87-90.

Codex ACC. (2003) Guidelines on Good Laboratory Practice in Residue Analysis. CAC/GL 40-1993, Rev.1-2003.

Coefficient_of_determination. In. 2017.

Cook J, Engel M, Wylie P, Quimby B. (1999) Multiresidue screening of pesticides in foods using retention time locking, GC-AED, database search, and GC/MS identification. *J AOAC Int*. 82:313-326.

Cunha SC, Fernandes JO, Alves A, Oliveira MBPP. (2009) Fast low-pressure gas chromatography–mass spectrometry method for the determination of multiple pesticides in grapes, musts and wines. *J Chromatogr A*. 1216:119-126.

Cycoń M, Wójcik M, Piotrowska-Seget Z. (2011) Biodegradation kinetics of the benzimidazole fungicide thiophanate-methyl by bacteria isolated from loamy sand soil. *Biodegradation*. 22:573-583.

Dass C. (2007) Tandem Mass Spectrometry, in Fundamentals of Contemporary Mass Spectrometry Hoboken, NJ, USA: John Wiley & Sons, Inc. p. 132-133.

de Sousa FA, Guido Costa AI, de Queiroz MELR, Teófilo RF, Neves AA, de Pinho GP. (2012) Evaluation of matrix effect on the GC response of eleven pesticides by PCA. *Food Chem*. 135:179-185.

Dias JV, Cutillas V, Lozano A, Pizzutti IR, Fernández-Alba AR. (2016) Determination of pesticides in edible oils by liquid chromatography-tandem mass spectrometry employing new generation materials for dispersive solid phase extraction clean-up. *J Chromatogr A*. 1462:8-18.

EN15662. (2008) Foods of plant origin-determination of pesticide residues using GC–MS and/or LC–MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE-QuEChERS-method. *EN 15662*. EN 15662.

Erney DR, Gillespie AM, Gilvydis DM, Poole CF. (1993) Explanation of the matrix-induced chromatographic response enhancement of organophosphorus pesticides during open tubular column gas chromatography with splitless or hot on-column injection and flame photometric detection. *J Chromatogr A*. 638:57-63.

Etxebarria N, Zuloaga O, Olivares M, Bartolomé LJ, Navarro P. (2009) Retention-time locked methods in gas chromatography. *J Chromatogr A*. 1216:1624-1629.

European Commission EU, European Union, European Commission. (2015). Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_11945.pdf

Fan S, Zhao P, Zhang F, Yu C, Pan C. (2013) Spinach or Amaranth May Represent Highest Residue of Thiophanate-Methyl with Open Field Application on Six Leaf Vegetables. *Bull Environ Contam Toxicol*. 90:477-481.

Ferrer C, Lozano A, Agüera A, Girón AJ, Fernández-Alba AR. (2011) Overcoming matrix effects using the dilution approach in multiresidue methods for fruits and vegetables. *J Chromatogr A*. 1218:7634-7639.

Fialkov AB, Steiner U, Jones L, Amirav A. (2006) A new type of GC–MS with advanced capabilities. *Int J Mass Spectrom*. 251:47-58.

García MDG, Duque SU, Fernández ABL, Sosa A, Fernández-Alba AR. (2017) Multiresidue method for trace pesticide analysis in honeybee wax comb by GC-QqQ-MS. *Talanta*. 163:54-64.

Geis-Asteggiante L, Lehotay SJ, Heinzen H. (2012) Effects of Temperature and Purity of Magnesium Sulfate During Extraction of Pesticide Residues Using the QuEChERS Method. *J AOAC Int*. 95:1311-1318.

Godula M, Hajšlová J, Alterová K. (1999) Pulsed splitless injection and the extent of matrix effects in the analysis of pesticides. *J High Resolut Chromatogr*. 22:395-402.

Golge O, Kabak B. (2015) Evaluation of QuEChERS sample preparation and liquid chromatography–triple-quadrupole mass spectrometry method for the determination of 109 pesticide residues in tomatoes. *Food Chem*. 176:319-332.

Grande-Martínez Á, Arrebola-Liébanas FJ, Martínez-Vidal JL, Hernández-Torres ME, Garrido-Frenich A. (2016) Optimization and validation of a multiresidue pesticide method in rice and wheat flour by modified QuEChERS and GC–MS/MS. *Food Anal Methods*. 9:548-563.

Grujic S, Vasiljevic T, Radisic M, Lausevic M. (2009) Determination of Pesticides by Matrix Solid-Phase Dispersion and Liquid Chromatography-Tandem Mass Spectrometry. In: *Handbook of Pesticides: Methods of Pesticide Residues Analysis.* FL, USA: CRC Pres.

Guan S-x, Yu Z-g, Yu H-n, Song C-h, Song Z-q, Qin Z. (2011) Multi-Walled Carbon Nanotubes as Matrix Solid-Phase Dispersion Extraction Adsorbent for Simultaneous Analysis of Residues of Nine Organophosphorus Pesticides in Fruit and Vegetables by Rapid Resolution LC–MS–MS. *Chromatographia*. 73:33-41.

Håkansson K, Chalmers MJ, Quinn JP, McFarland MA, Hendrickson CL, Marshall AG. (2003) Combined Electron Capture and Infrared Multiphoton Dissociation for Multistage MS/MS in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. *Anal Chem*. 75:3256-3262.

Hajšlová J, Holadová K, Kocourek V, Poustka J, Godula M, Cuhra P, et al. (1998) Matrix-induced effects: a critical point in the gas chromatographic analysis of pesticide residues. *J Chromatogr A*. 800:283-295.

Han L, Matarrita J, Sapozhnikova Y, Lehotay SJ. (2016) Evaluation of a recent product to remove lipids and other matrix co-extractives in the analysis of pesticide residues and environmental contaminants in foods. *J Chromatogr A*. 1449:17-29.

Han Y, Song L, Zou N, Chen R, Qin Y, Pan C. (2016) Multi-residue determination of 171 pesticides in cowpea using modified QuEChERS method with multi-walled carbon nanotubes as reversed-dispersive solid-phase extraction materials. *J Chromatogr B*. 1031:99-108.

Han Y, Song L, Zou N, Qin Y, Li X, Pan C. (2017) Rapid multiplug filtration cleanup method for the determination of 124 pesticide residues in rice, wheat, and corn. *J Sep Sci*. 40:878-884.

Hanot V, Goscinny S, Deridder M. (2015) A simple multi-residue method for the determination of pesticides in fruits and vegetables using a methanolic extraction and ultra-high-performance liquid chromatography-tandem mass

spectrometry: optimization and extension of scope. *J Chromatogr A*. 1384:53-66.

Hayward DG, Wong JW, Park HY. (2015) Determinations for pesticides on black, green, oolong, and white teas by gas chromatography triple-quadrupole mass spectrometry. *J Agric Food Chem*. 63:8116-8124.

Hayward DG, Wong JW, Shi F, Zhang K, Lee NS, DiBenedetto AL, et al. (2013) Multiresidue Pesticide Analysis of Botanical Dietary Supplements Using Salt-out Acetonitrile Extraction, Solid-Phase Extraction Cleanup Column, and Gas Chromatography–Triple Quadrupole Mass Spectrometry. *Anal Chem*. 85:4686-4693.

He Z, Chen S, Wang L, Peng Y, Luo M, Wang W, et al. (2015) Multiresidue analysis of 213 pesticides in leek and garlic using QuEChERS-based method and gas chromatography-triple quadrupole mass spectrometry. *Analytical and Bioanalytical Chemistry*. 407:2637-2643.

He Z, Wang L, Peng Y, Luo M, Wang W, Liu X. (2015) Multiresidue analysis of over 200 pesticides in cereals using a QuEChERS and gas chromatography–tandem mass spectrometry-based method. *Food Chem*. 169:372-380.

Holmes B, Dunkin A, Schoen R, Wiseman C. (2015) single-laboratory ruggedness testing and validation of a modified QuEChERS approach To quantify 185 pesticide residues in salmon by liquid chromatography– and gas chromatography–tandem mass spectrometry. *J Agric Food Chem*. 63:5100-5106.

Hou X, Lei S, Guo L, Qiu S. (2016) Optimization of a multi-residue method for 101 pesticides in green tea leaves using gas chromatography–tandem mass spectrometry. *Rev Bras Farmacogn*. 26:401-407.

http://quechers.cvua-stuttgart.de, (2011). QuEChERS. http://quechers.cvua-stuttgart.de/index.php?nav1o=2&nav2o=1&nav3o=0

Huber L. (2010) Validation of Analytical Methods. *Agilent*. 5990-5140EN.

Hughes NC, Wong EYK, Fan J, Bajaj N. (2007) Determination of carryover and contamination for mass spectrometry-based chromatographic assays. *The AAPS Journal*. 9:E353-E360.

Introduction to LC-MS. http://www.shimadzu.com. (2017). http://www.shimadzu.com/an/hplc/support/lib/lctalk/47/47intro.html

IUPAC, Blackwell Scientific Publication. (1997). Compendium of Chemical Terminology. http://goldbook.iupac.org/html/T/T06250.html

Jadhav MR, Oulkar DP, Shabeer T. P A, Banerjee K. (2015) Quantitative screening of agrochemical residues in fruits and vegetables by buffered ethyl acetate extraction and LC-MS/MS analysis. *J Agric Food Chem*. 63:4449-4456.

Johnson JV, Yost RA, Kelley PE, Bradford DC. (1990) Tandem-in-space and tandem-in-time mass spectrometry: triple quadrupoles and quadrupole ion traps. *Analytical Chemistry*. 62:2162-2172.

Jones RL, Hunt TW, Norris FA, Harden CF. (1989) Field research studies on the movement and degradation of thiodicarb and its metabolite methomyl. *J Contam Hydrol*. 4:359-371.

Kaczynski P. (2017) Clean-up and matrix effect in LC-MS/MS analysis of food of plant origin for high polar herbicides. *Food Chem*. 230:524-531.

Kaczyński P. (2017) Large-scale multi-class herbicides analysis in oilseeds by rapid one-step QuEChERS-based extraction and cleanup method using liquid chromatography–tandem mass spectrometry. *Food Chem*. 230:411-422.

Kaczynski P, Hrynko I, Lozowicka B. (2017) Evolution of novel sorbents for effective clean-up of honeybee matrix in highly toxic insecticide LC/MS/MS analysis. *Ecotoxicol Environ Saf*. 139:124-131.

Kaczyński P, Łozowicka B. (2017) One-Step QuEChERS-Based Approach to Extraction and Cleanup in Multiresidue Analysis of Sulfonylurea Herbicides in Cereals by Liquid Chromatography–Tandem Mass Spectrometry. *Food Anal Methods*. 10:147-160.

Kaczyński P, Łozowicka B, Perkowski M, Szabuńko J. (2017) Multiclass pesticide residue analysis in fish muscle and liver on one-step extraction-cleanup strategy coupled with liquid chromatography tandem mass spectrometry. *Ecotoxicol Environ Saf*. 138:179-189.

Kaplan DA, Hartmer R, Speir JP, Stoermer C, Gumerov D, Easterling ML, et al. (2008) Electron transfer dissociation in the hexapole collision cell of a hybrid quadrupole-hexapole Fourier transform ion cyclotron resonance mass spectrometer. *Rapid Communications in Mass Spectrometry*. 22:271-278.

Khan ZS, Girame R, Utture SC, Ghosh RK, Banerjee K. (2015) Rapid and sensitive multiresidue analysis of pesticides in tobacco using low pressure and traditional gas chromatography tandem mass spectrometry. *Journal of Chromatography A*. 1418:228-232.

Kiljanek T, Niewiadowska A, Gaweł M, Semeniuk S, Borzęcka M, Posyniak A, et al. (2017) Multiple pesticide residues in live and poisoned honeybees – Preliminary exposure assessment. *Chemosphere*. 175:36-44.

Kiljanek T, Niewiadowska A, Semeniuk S, Gaweł M, Borzęcka M, Posyniak A. (2016) Multi-residue method for the determination of pesticides and pesticide metabolites in honeybees by liquid and gas chromatography coupled with tandem mass spectrometry—Honeybee poisoning incidents. *J Chromatogr A*. 1435:100-114.

King R, Bonfiglio R, Fernandez-Metzler C, Miller-Stein C, Olah T. (2000) Mechanistic investigation of ionization suppression in electrospray ionization. *J Am Soc Mass Spectrom*. 11:942-950.

Kittlaus S, Schimanke J, Kempe G, Speer K. (2011) Assessment of sample cleanup and matrix effects in the pesticide residue analysis of foods using postcolumn infusion in liquid chromatography–tandem mass spectrometry. *J Chromatogr A*. 1218:8399-8410.

Koesukwiwat U, Lehotay SJ, Leepipatpiboon N. (2011) Fast, low-pressure gas chromatography triple quadrupole tandem mass spectrometry for analysis of 150 pesticide residues in fruits and vegetables. *Journal of Chromatography A*. 1218:7039-7050.

Koesukwiwat U, Lehotay SJ, Miao S, Leepipatpiboon N. (2010) High throughput analysis of 150 pesticides in fruits and vegetables using QuEChERS and low-

pressure gas chromatography–time-of-flight mass spectrometry. *J Chromatogr A*. 1217:6692-6703.

Koesukwiwat U, Sanguankaew K, Leepipatpiboon N. (2008) Rapid determination of phenoxy acid residues in rice by modified QuEChERS extraction and liquid chromatography–tandem mass spectrometry. *Anal Chim Acta*. 626:10-20.

Konstantinou JK. (2015) Mass Spectrometric Techniques for the Determination of Pesticide Transformation Products Formed by Advanced Oxidation Processes. In: *Mass Spectrometry for the Analysis of Pesticide Residues alid Their Metabolites*. First Edition ed.: John Wiley & Sons, Inc. p. 231-259.

Korean Pesticides MRLs in Food; 2016;. In. 2016.

Kováts E. (1958) Gas-chromatographische charakterisierung organischer verbindungen. Teil 1: retentionsindices aliphatischer halogenide, alkohole, aldehyde und ketone. *Helvetica Chimica Acta*. 41:1915-1932.

Kwon H, Lehotay SJ, Geis-Asteggiante L. (2012) Variability of matrix effects in liquid and gas chromatography–mass spectrometry analysis of pesticide residues after QuEChERS sample preparation of different food crops. *J Chromatogr A*. 1270:235-245.

López-Blanco R, Nortes-Méndez R, Robles-Molina J, Moreno-González D, Gilbert-López B, García-Reyes JF, et al. (2016) Evaluation of different cleanup sorbents for multiresidue pesticide analysis in fatty vegetable matrices by liquid chromatography tandem mass spectrometry. *Journal of Chromatography A*. 1456:89-104.

Lee J, Kim L, Shin Y, Lee J, Lee J, Kim E, et al. (2017) Rapid and simultaneous analysis of 360 pesticides in brown rice, spinach, orange, and potato using microbore GC-MS/MS. *J Agric Food Chem*. 65:3387-3395.

Lehotay SJ. (2007) Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: collaborative study. *J AOAC Int*. 90:485-520.

Lehotay SJ, Maštovská K, Lightfield AR. (2005) Use of buffering and other means to improve results of problematic pesticides in a fast and easy method for residue analysis of fruits and vegetables. *J AOAC Int*. 88:615-629.

Lehotay SJ, Mastovska K, Yun SJ. (2005) Evaluation of two fast and easy methods for pesticide residue analysis in fatty food matrixes. *J AOAC Int*. 88:630-638.

Li L, Li W, Qin D, Jiang S, Liu F. (2009) Application of graphitized carbon black to the QuEChERS method for pesticide multiresidue analysis in spinach. *J AOAC Int*. 92:538-547.

Li Y-F, Qiao L-Q, Li F-W, Ding Y, Yang Z-J, Wang M-L. (2014) Determination of multiple pesticides in fruits and vegetables using a modified quick, easy, cheap, effective, rugged and safe method with magnetic nanoparticles and gas chromatography tandem mass spectrometry. *J Chromatogr A*. 1361:77-87.

Li Y, Kelley RA, Anderson TD, Lydy MJ. (2015) Development and comparison of two multi-residue methods for the analysis of select pesticides in honey bees, pollen, and wax by gas chromatography–quadrupole mass spectrometry. *Talanta*. 140:81-87.

Lin J-M, Liu L-B, Liu Y. (2009) Determination of Pesticide Residues in Fruits and Vegetables by Using GC/MS and LC/MS. In: *Handbook of Pesticides*. CRC Press. p. 497-523.

Liu L-B, Liu Y, Lin J-M. (2016) Determination of pesticide residues in fruits and vegetables by using GC-MS ad LC-MS. In: *Handbook of Pesticides: Methods of Pesticide Residues Analysis*. CRC Press. p. 497-520.

Liu S, Huang X, Jin Q, Zhu G. (2017a) Determination of a broad spectrum of endocrine-disrupting pesticides in fish samples by UHPLC-MS/MS using the pass-through cleanup approach. *J Sep Sci*. 40:1266-1272.

Liu S, Huang X, Jin Q, Zhu G. (2017b) Determination of a broad spectrum of endocrine-disrupting pesticides in fish samples by UHPLC–MS/MS using the pass-through cleanup approach. *Journal of Separation Science*. 40:1266-1272.

Liu XQ, Li YF, Meng WT, Li DX, Sun H, Tong L, et al. (2016) A multi-residue method for simultaneous determination of 74 pesticides in Chinese material medica using modified QuEChERS sample preparation procedure and gas chromatography tandem mass spectrometry. *J Chromatogr B Analyt Technol Biomed Life Sci*. 1015-1016:1-12.

Lozano A, Kiedrowska B, Scholten J, de Kroon M, de Kok A, Fernández-Alba AR. (2016) Miniaturisation and optimisation of the Dutch mini-Luke extraction method for implementation in the routine multi-residue analysis of pesticides in fruits and vegetables. *Food Chem*. 192:668-681.

Lozano A, Kiedrowska B, Scholten J, de Kroon M, de Kok A, Fernandez-Alba AR. (2016) Miniaturisation and optimisation of the Dutch mini-Luke extraction method for implementation in the routine multi-residue analysis of pesticides in fruits and vegetables. *Food Chem*. 192:668-681.

Lozano A, Rajski Ł, Uclés S, Belmonte-Valles N, Mezcua M, Fernández-Alba AR. (2014) Evaluation of zirconium dioxide-based sorbents to decrease the matrix effect in avocado and almond multiresidue pesticide analysis followed by gas chromatography tandem mass spectrometry. *Talanta*. 118:68-83.

Lozowicka B, Ilyasova G, Kaczynski P, Jankowska M, Rutkowska E, Hrynko I, et al. (2016) Multi-residue methods for the determination of over four hundred pesticides in solid and liquid high sucrose content matrices by tandem mass spectrometry coupled with gas and liquid chromatograph. *Talanta*. 151:51-61.

Lucero M, Estell R, Tellez M, Fredrickson E. (2009) A retention index calculator simplifies identification of plant volatile organic compounds. *Phytochemical Analysis*. 20:378-384.

Machado I, Gérez N, Pistón M, Heinzen H, Cesio MV. (2017) Determination of pesticide residues in globe artichoke leaves and fruits by GC–MS and LC–MS/MS using the same QuEChERS procedure. *Food Chemistry*. 227:227-236.

Martínez-Domínguez G, Nieto-García AJ, Romero-González R, Frenich AG. (2015) Application of QuEChERS based method for the determination of pesticides in nutraceutical products (Camellia sinensis) by liquid chromatography coupled to triple quadrupole tandem mass spectrometry. *Food Chem*. 177:182-190.

Mastovská K, Lehotay SJ. (2003) Practical approaches to fast gas chromatography-mass spectrometry. *J Chromatogr A*. 1000:153-180.

Maštovská K, Lehotay SJ, Anastassiades M. (2005) Combination of Analyte Protectants To Overcome Matrix Effects in Routine GC Analysis of Pesticide Residues in Food Matrixes. *Anal Chem*. 77:8129-8137.

Matuszewski BK, Constanzer ML, Chavez-Eng CM. (2003) Strategies for the Assessment of Matrix Effect in Quantitative Bioanalytical Methods Based on HPLC−MS/MS. *Anal Chem*. 75:3019-3030.

Mol HGJ, Rooseboom A, van Dam R, Roding M, Arondeus K, Sunarto S. (2007) Modification and re-validation of the ethyl acetate-based multi-residue method for pesticides in produce. *Anal Bioanal Chem*. 389:1715-1754.

Morris BD, Schriner RB. (2015) Development of an automated column solid-phase extraction cleanup of QuEChERS extracts, using a zirconia-based sorbent, for pesticide residue analyses by LC-MS/MS. *J Agric Food Chem*. 63:5107-5119.

Murray Kermit K, Boyd Robert K, Eberlin Marcos N, Langley GJ, Li L, Naito Y. 2013. Definitions of terms relating to mass spectrometry (IUPAC Recommendations 2013). In: Pure and Applied Chemistry. p. 1515.

NATA. (2012) Guidelines for the validation and verification of quantitative and qualitative test methods. *National Association of Testing Authorities, Australia*. Technical Note 17.

Nie J, Miao S, Lehotay SJ, Li W-T, Zhou H, Mao X-H, et al. (2015) Multi-residue analysis of pesticides in traditional Chinese medicines using gas chromatography-negative chemical ionisation tandem mass spectrometry. *Food Additives & Contaminants: Part A*. 32:1287-1300.

Nie J, Shui Miao, Steven J. Lehotay, Wen-Ting Li, Heng Zhou, Xiu-Hong Mao, et al. (2015) Multi-residue analysis of pesticides in traditional Chinese medicines using gas chromatography-negative chemical ionisation tandem mass spectrometry. *Food Addit Contam, Part A*. 32:1287-1300.

Niell S, Cesio V, Hepperle J, Doerk D, Kirsch L, Kolberg D, et al. (2014) QuEChERS-based method for the multiresidue analysis of pesticides in beeswax by LC-MS/MS and GC×GC-TOF. *J Agric Food Chem*. 62:3675-3683.

Nieto-García AJ, Romero-González R, Garrido Frenich A. (2015) Multi-pesticide residue analysis in nutraceuticals from grape seed extracts by gas chromatography coupled to triple quadrupole mass spectrometry. *Food Control*. 47:369-380.

OECD. (2007) Guidance document on pesticide residue analytical methods. ENV/JM/MONO(2007)17.

Palenikova A, Martinez-Dominguez G, Arrebola FJ, Romero-Gonzalez R, Hrouzkova S, Frenich AG. (2015) Multifamily determination of pesticide residues in soya-based nutraceutical products by GC/MS-MS. *Food Chem*. 173:796-807.

Pang G-F, Cao Y-Z, Fan C-L, Jia G-Q, Zhang J-J, Li X-M, et al. (2009) Analysis Method Study on 839 Pesticide and Chemical Contaminant Multiresidues in Animal Muscles by Gel Permeation Chromatography Cleanup, GC/MS, and LC/MS/MS. *Journal of AOAC International*. 92:S1-S72.

Particle-Sciences. 2009. Mass Spectrometry in Bioanalysis. Technical Brief: 2009: Volume 4 Sect. Section|:Start Page| (col. Column)|.

Patel K, Fussell RJ, Hetmanski M, Goodall DM, Keely BJ. (2005) Evaluation of gas chromatography-tandem quadrupole mass spectrometry for the determination of organochlorine pesticides in fats and oils. *J Chromatogr A*. 1068:289-296.

Peruga A, Barreda M, Beltrán J, Hernández F. (2013) A robust GC-MS/MS method for the determination of chlorothalonil in fruits and vegetables. *Food Addit Contam, Part A*. 30:298-307.

Petrarca MH, Ccanccapa-Cartagena A, Masiá A, Godoy HT, Picó Y. (2017) Comparison of green sample preparation techniques in the analysis of pyrethrins and pyrethroids in baby food by liquid chromatography–tandem mass spectrometry. *J Chromatogr A*. 1497:28-37.

Qin Y, Zhang J, Zhang Y, Li F, Han Y, Zou N, et al. (2016) Automated multi-plug filtration cleanup for liquid chromatographic–tandem mass spectrometric pesticide multi-residue analysis in representative crop commodities. *J Chromatogr A*. 1462:19-26.

Rahman MM, Abd El-Aty AM, Shim J-H. (2013) Matrix enhancement effect: A blessing or a curse for gas chromatography?—A review. *Anal Chim Acta*. 801:14-21.

Rajski Ł, Lozano A, Uclés A, Ferrer C, Fernández-Alba AR. (2013) Determination of pesticide residues in high oil vegetal commodities by using various multi-residue methods and clean-ups followed by liquid chromatography tandem mass spectrometry. *J Chromatogr A*. 1304:109-120.

Rasche C, Fournes B, Dirks U, Speer K. (2015) Multi-residue pesticide analysis (gas chromatography–tandem mass spectrometry detection)—Improvement of the quick, easy, cheap, effective, rugged, and safe method for dried fruits and fat-rich cereals—Benefit and limit of a standardized apple purée calibration (screening). *J Chromatogr A*. 1403:21-31.

Ravelo-Pérez LM, Hernández-Borges J, Rodríguez-Delgado MÁ. (2008) Multi-walled carbon nanotubes as efficient solid-phase extraction materials of organophosphorus pesticides from apple, grape, orange and pineapple fruit juices. *J Chromatogr A*. 1211:33-42.

Regueiro J, Negreira N, Hannisdal R, Berntssen MHG. (2017) Targeted approach for qualitative screening of pesticides in salmon feed by liquid chromatography coupled to traveling-wave ion mobility/quadrupole time-of-flight mass spectrometry. *Food Control*. 78:116-125.

Rejczak T, Tuzimski T. 2015. A review of recent developments and trends in the QuEChERS sample preparation approach. In: Open Chemistry.

Ribeiro Begnini Konatu F, Breitkreitz MC, Sales Fontes Jardim IC. (2017) Revisiting quick, easy, cheap, effective, rugged, and safe parameters for sample preparation in pesticide residue analysis of lettuce by liquid chromatography–tandem mass spectrometry. *J Chromatogr A*. 1482:11-22.

Rizzetti TM, Kemmerich M, Martins ML, Prestes OD, Adaime MB, Zanella R. (2016) Optimization of a QuEChERS based method by means of central composite design for pesticide multiresidue determination in orange juice by UHPLC–MS/MS. *Food Chem*. 196:25-33.

Rossi S-A, Johnson JV, Yost RA. (1992) Optimization of short-column gas chromatography/electron ionization mass spectrometry conditions for the

determination of underivatized anabolic steroids. *Biological Mass Spectrometry*. 21:420-430.

Rostom AA, Fucini P, Benjamin DR, Juenemann R, Nierhaus KH, Hartl FU, et al. (2000) Detection and selective dissociation of intact ribosomes in a mass spectrometer. *Proceedings of the National Academy of Sciences*. 97:5185-5190.

Sack C, Vonderbrink J, Smoker M, Smith RE. (2015) Determination of acid herbicides using modified QuEChERS with fast switching ESI+/ESI– LC-MS/MS. *J Agric Food Chem*. 63:9657-9665.

Sannino A. (2008) Food contaminants and residue analysis. In: *Comprehensive Analytical Chemistry*. 1st ed ed. Amsterdam, The Netherlands: Elsevier.

Sargent [ED] M. 2013. Guide to achieving reliable

quantitative

LC-MS measurements. Sect. Section|:Start Page| (col. Column)|.

Sargent M. (2013) Guide to achieving reliable quantitative LC-MS measurements: RSC Analytical Methods Committee.

Savant RH, Banerjee K, Utture SC, Patil SH, Dasgupta S, Ghaste MS, et al. (2010) Multiresidue Analysis of 50 Pesticides in Grape, Pomegranate, and Mango by Gas Chromatography−Ion Trap Mass Spectrometry. *J Agric Food Chem*. 58:1447-1454.

Schenck FJ, Lehotay SJ. (2000) Does further clean-up reduce the matrix enhancement effect in gas chromatographic analysis of pesticide residues in food? *J Chromatogr A*. 868:51-61.

Shabir GA. (2003) Validation of high-performance liquid chromatography methods for pharmaceutical analysis: Understanding the differences and similarities between validation requirements of the US Food and Drug Administration, the US Pharmacopeia and the International Conference on Harmonization. *J Chromatogr A*. 987:57-66.

Shah VP, Midha KK, Findlay JWA, Hill HM, Hulse JD, McGilveray IJ, et al. (2000) Bioanalytical Method Validation—A Revisit with a Decade of Progress. *Pharmaceutical Research*. 17:1551-1557.

Shendy AH, Al-Ghobashy MA, Mohammed MN, Gad Alla SA, Lotfy HM. (2016) Simultaneous determination of 200 pesticide residues in honey using gas chromatography–tandem mass spectrometry in conjunction with streamlined quantification approach. *J Chromatogr A*. 1427:142-160.

Shimelis O, Yang Y, Stenerson K, Kaneko T, Ye M. (2007) Evaluation of a solid-phase extraction dual-layer carbon/primary secondary amine for clean-up of fatty acid matrix components from food extracts in multiresidue pesticide analysis. *J Chromatogr A*. 1165:18-25.

Sivaperumal P, Anand P, Riddhi L. (2015) Rapid determination of pesticide residues in fruits and vegetables, using ultra-high-performance liquid chromatography/time-of-flight mass spectrometry. *Food Chem*. 168:356-365.

Soboleva E, Rathor N, Mageto A, Ambrus A. (2000) Estimation of significance of 'matrix-induced' chromatographic effects. In: *Principles and Practices of Method Validation*. The Royal Society of Chemistry. p. 138-156.

Stachniuk A, Fornal E. (2016) Liquid Chromatography-Mass Spectrometry in the Analysis of Pesticide Residues in Food. *Food Anal Methods*. 9:1654-1665.

Stachniuk A, Szmagara A, Czeczko R, Fornal E. (2017) LC-MS/MS determination of pesticide residues in fruits and vegetables. *J Environ Sci Health, Part B*.1-12.

Stahnke H, Alder L. (2015) Matrix Effects in Liquid Chromatography-Eiectrospray Ionization-Mass Spectrometry. In: *Mass Spectrometry for the Analysis of Pesticide Residues and Their Metabolites*. Hoboken, New Jersey: John Wiley & Sons, Inc.

Stahnke H, Kittlaus S, Kempe G, Alder L. (2012) Reduction of Matrix Effects in Liquid Chromatography–Electrospray Ionization–Mass Spectrometry by Dilution of the Sample Extracts: How Much Dilution is Needed? *Anal Chem*. 84:1474-1482.

Tsipi D, Botitsi H, Economou A. (2015) Legislation, Monitoring, and Analytical Quality Control for Pesticide Residues. In: *Mass Spectrometry for the Analysis of Pesticide Residues and Their Metabolites*. John Wiley & Sons, Inc. p. 35-52.

Uclés S, Belmonte N, Mezcua M, Martínez AB, Martinez-Bueno MJ, Gamón M, et al. (2014) Validation of a multiclass multiresidue method and monitoring results for 210 pesticides in fruits and vegetables by gas chromatography-triple quadrupole mass spectrometry. *J Environ Sci Health, Part B*. 49:557-568.

Uclés S, Uclés A, Lozano A, Martínez Bueno MJ, Fernández-Alba AR. (2017) Shifting the paradigm in gas chromatography mass spectrometry pesticide analysis using high resolution accurate mass spectrometry. *J Chromatogr A*. 1501:107-116.

Ucles S, Belmonte N, Mezcua M, Martinez AB, Martinez-Bueno MJ, Gamon M, et al. (2014) Validation of a multiclass multiresidue method and monitoring results for 210 pesticides in fruits and vegetables by gas chromatography-triple quadrupole mass spectrometry. *J Environ Sci Health B*. 49:557-568.

Unsworth J, IUPAC. (2010). RESIDUE ANALYTICAL METHODS. http://agrochemicals.iupac.org/index.php?option=com_sobi2&sobi2Task=sobi2Details&catid=7&sobi2Id=13

Vázquez PP, Lozano A, Uclés S, Ramos MMG, Fernández-Alba AR. (2015) A sensitive and efficient method for routine pesticide multiresidue analysis in bee pollen samples using gas and liquid chromatography coupled to tandem mass spectrometry. *Journal of Chromatography A*. 1426:161-173.

Van Den Dool H, Dec. Kratz P. (1963) A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *J Chromatogr A*. 11:463-471.

Van Eeckhaut A, Lanckmans K, Sarre S, Smolders I, Michotte Y. (2009) Validation of bioanalytical LC–MS/MS assays: Evaluation of matrix effects. *J Chromatogr B*. 877:2198-2207.

Vazquez PP, Lozano A, Ucles S, Ramos MM, Fernandez-Alba AR. (2015) A sensitive and efficient method for routine pesticide multiresidue analysis in bee pollen samples using gas and liquid chromatography coupled to tandem mass spectrometry. *J Chromatogr A*. 1426:161-173.

Walorczyk S. (2007) Development of a multi-residue screening method for the determination of pesticides in cereals and dry animal feed using gas chromatography–triple quadrupole tandem mass spectrometry. *J Chromatogr A*. 1165:200-212.

Walorczyk S. (2008) Application of gas chromatography/tandem quadrupole mass spectrometry to the multi-residue analysis of pesticides in green leafy vegetables. *Rapid Communications in Mass Spectrometry*. 22:3791-3801.

Walorczyk S, Drożdżyński D. (2012) Improvement and extension to new analytes of a multi-residue method for the determination of pesticides in cereals and dry animal feed using gas chromatography–tandem quadrupole mass spectrometry revisited. *J Chromatogr A*. 1251:219-231.

Walorczyk S, Drożdżyński D, Kierzek R. (2015a) Determination of pesticide residues in samples of green minor crops by gas chromatography and ultra performance liquid chromatography coupled to tandem quadrupole mass spectrometry. *Talanta*. 132:197-204.

Walorczyk S, Drożdżyński D, Kierzek R. (2015b) Two-step dispersive-solid phase extraction strategy for pesticide multiresidue analysis in a chlorophyll-containing matrix by gas chromatography–tandem mass spectrometry. *J Chromatogr A*. 1412:22-32.

Walorczyk S, Gnusowski B. (2009) Development and validation of a multi-residue method for the determination of pesticides in honeybees using acetonitrile-based extraction and gas chromatography-tandem quadrupole mass spectrometry. *J Chromatogr A*. 1216:6522-6531.

Wang X, Qi P, Wang X, Zhang Q, Wang Z, Xu X, et al. (2017) An efficient cleanup method coupled with gas chromatography and mass spectrometry for multi-pesticides residue analysis in complex plant matrices. *Journal of Separation Science*.n/a-n/a.

Wong JW, Zhang K, Tech K, Hayward DG, Makovi CM, Krynitsky AJ, et al. (2010) Multiresidue pesticide analysis in fresh produce by capillary gas chromatography−mass spectrometry/selective ion monitoring (GC-MS/SIM) and −tandem mass spectrometry (GC-MS/MS). *J Agric Food Chem*. 58:5868-5883.

Wu C-C. (2017) Multiresidue method for the determination of pesticides in Oolong tea using QuEChERS by gas chromatography-triple quadrupole tandem mass spectrometry. *Food Chem*. 229:580-587.

Wu Y, Liu X, Dong F, Xu J, Yan Z, Wu X, et al. (2013) Simultaneous determination of thiodicarb and its main metabolite residues in cotton by ultra-performance liquid chromatography coupled to tandem mass spectrometry. *Anal Methods*. 5:1052-1057.

Wylie PL. (1996) Improved gas chromatographic analysis of organophosphorus pesticides with pulsed splitless injection. *J AOAC Int*. 79:571-577.

Yang P, Chang JS, Wong JW, Zhang K, Krynitsky AJ, Bromirski M, et al. (2015) Effect of sample dilution on matrix effects in pesticide analysis of several matrices by liquid chromatography-high-resolution mass spectrometry. *J Agric Food Chem*. 63:5169-5177.

Zhang Z, Feng M, Zhu K, Han L, Sapozhnikova Y, Lehotay SJ. (2016) Multiresidue Analysis of Pesticides in Straw Roughage by Liquid Chromatography–Tandem Mass Spectrometry. *J Agric Food Chem*. 64:6091-6099.

Zhao M-A, Feng Y-N, Zhu Y-Z, Kim J-H. (2014) Multi-residue Method for Determination of 238 Pesticides in Chinese Cabbage and Cucumber by Liquid Chromatography–Tandem Mass Spectrometry: Comparison of Different Purification Procedures. *Journal of Agricultural and Food Chemistry*. 62:11449-11456.

Zhao P, Huang B, Li Y, Han Y, Zou N, Gu K, et al. (2014) Rapid multiplug filtration cleanup with multiple-walled carbon nanotubes and gas chromatography-triple-quadruple mass spectrometry detection for 186 pesticide residues in tomato and tomato products. *J Agric Food Chem*. 62:3710-3725.

Zhao P, Wang L, Zhou L, Zhang F, Kang S, Pan C. (2012) Multi-walled carbon nanotubes as alternative reversed-dispersive solid phase extraction materials in pesticide multi-residue analysis with QuEChERS method. *J Chromatogr A*. 1225:17-25.

Zou N, Han Y, Li Y, Qin Y, Gu K, Zhang J, et al. (2016) Multiresidue Method for Determination of 183 Pesticide Residues in Leeks by Rapid Multiplug Filtration Cleanup and Gas Chromatography–Tandem Mass Spectrometry. *J Agric Food Chem*. 64:6061-6070.

Zrostlíková J, Lehotay SJ, Hajšlová J. (2002) Simultaneous analysis of organophosphorus and organochlorine pesticides in animal fat by gas chromatography with pulsed flame photometric and micro-electron capture detectors. *J Sep Sci*. 25:527-537.

Abstract in Korean

인간에게 있어서 농약은 식량확보에 필수 불가결한 물질로서 처리 후 잔류된 농약은 잠재적으로 인체 건강과 밀접히 연관되어 있다. 따라서, 농산물 및 식품 중 잔류농약 분석은 한치의 관용도 인정되지 않도록 엄격하고 빈틈없이 수행되어야 한다. 또한 수입농산물과 신규농약 및 미등록 농약이 늘어나고 있는 상황에서 빠르고 정확한, 그리고 한번에 많은 수의 농약을 분석하는 동시 다성분 잔류농약 분석은 분석 연구자에게 늘 과제로 여겨져 왔다. 본 연구에서는 500 여종의 농약성분에 대하여 개선된 QuEChERS 전처리법과 기체크로마토그래피 및 액체크로마토그래피-탠덤질량분석기 (GC-MS/MS 와 LC-MS/MS)를 이용하여 간단하고 빠른 농약 다성분 동시 분석법을 확립하였다. GC 및 LC 에 적용이 가능하고 다양한 물리화학적 성질을 지닌 농약성분들의 MS/MS 분석에서의 최적의 감도와 선택성을 확보하기 위하여, 충돌에너지, 선구 이온 및 토막이온 과 같은 다중반응검지법 (Multiple Reaction Monitoring, MRM) 조건 들을 최적화하였다. 360 개 농약의 GC-MS/MS 분석을 위하여, 짧고 (길이 20 m) 가는 (내경 0.18 mm) microbore 컬럼을 적용하였고, 그 결과 기존 narrowbore 분석컬럼 (길이 30m, 내경 0.25 mm)에 비하여 짧아진 분석시간과 함께 각 피크에서 향상된 신호대 잡음비(S/N)를 얻을 수 있었다. 또한 펄스압력 주입법 (pulsed pressure injection)은 GC-MS/MS 에서 감도와 S/N 비를 향상 시키는데 기여하였으며, 새로운 라이너 교체 후의 프라이밍 주입은 매질효과에 의한 감도저하 현상을 방지하여 높은 감도를 유지하는 데에 큰 역할을 하는 것으로 밝혀졌다. LC-MS/M 을 이용한 332 개 농약 분석을 위하여 최적의 용매 조성을 선정하였고, 시료 주입량과 기기 재현성 관계를 규명하여 최적의 감도와 재현성을 확보 하고자 하였다. 시료의 전처리를 위하여, 추가적인 버퍼없이 0.1% 포름산 함유 아세토니트릴로 추출 및

분배하였고, 정제법으로는 많은 농약의 회수율이 양호했던 일차-이차 아민이 함유된 분산 고체상 추출법이 사용되었다. 대부분의 성분에서 검출한계 0.01 mg/kg 이하와 >0.99 이상의 검량선 직선성을 얻을 수 있었다. 최적화된 분석법을 이용하여 유럽연합의 농약분석법 검증 가이드 라인에 따라, 0.01 과 0.05 mg/kg 두 수준에서 6 반복 회수율 시험을 수행하였으며, 대부분의 농약이 회수율 수준 70-120%, 분석오차 20%이내를 만족하여, 정확도와 재현성을 만족함을 확인하였다. 또한 개발된 분석법을 실제 시료에 성공적으로 적용하여, 일상분석에서 활용에 문제가 없음을 확인하였다.

주요어: 감자, 기체크로마토그래피-탠덤질량분석기, 농약 동시다성분 분석법, 액체크로마토그래피-탠덤질량분석기, 오렌지, 시금치, 현미

학 번: 2013-30354

Literature Contributions

Journal publication

1) **Jonghwa Lee**, Yongho Shin, Junghak Lee, Jiho Lee, Eunhye Kim, and Jeong-Han Kim, "Sensitivity enhancement using a microbore column and pulsed pressure injection in the simultaneous analysis of 356 pesticide multiresidues by gas chromatography-tandem mass spectrometry", ***Journal of Applied Biological Chemistry***, 2017, 13 June (Published online)

2) **Jonghwa Lee**, Leesun Kim, Yongho Shin, Junghak Lee, Jiho Lee, Eunhye Kim, Joon-Kwan Moon, and Jeong-Han Kim, "Rapid and Simultaneous Analysis of 360 Pesticides in Brown Rice, Spinach, Orange, and Potato using Microbore GC-MS/MS", ***Journal of Agricultural and Food Chemistry***, 2017, 65 (16), pp 3387–3395, 27 Mar 2017

3) Jimi Cho, **Jonghwa Lee**, Chai-Uk Lim & Jongsung Ahn, "Quantification of pesticides in food crops using QuEChERS approaches and GC-MS/MS", ***Food Additives & Contaminants: Part A***, 2016, 33(12), 1803–1816, 17 Nov 2016

4) H. Lee, J.-H. Kim, E. Kim, Y. Shin, **J.-H. Lee**, H.Jung, Y.Lim, H. S. Lee, J.-H. Kim, "Biotransformation and Molecular Docking of Cyazofamid by Human Liver Microsomes and cDNA-expressed Human Recombinant P450s", ***Journal of Applied Biological Chemistry***, 59(4): 649-653, August 2016

5) Hyeri Lee, Eunhye Kim, Yongho Shin, **Jong-Hwa Lee**, Hor-Gil Hur, Jeong-Han Kim, "Identification and formation pattern of metabolites of cyazofamid by soil fungus Cunninghamella elegans", ***Journal of Applied Biological Chemistry***, 59(1): 9-14, Jan 2016

6) Hyeri Lee, Eunhye Kim, **Jong-Hwa Lee**, Jeong Hee Sung, Hoon Choi, Jeong-Han Kim, "Analysis of Cyazofamid and its Metabolite in the Environmental and Crop Samples Using LC–MS/MS", ***Bulletin of environmental contamination and toxicology***, 93(5), 586-590, August 2014

Oral presentations (International)

1) **Jonghwa Lee**, Yongho Shin, Jung Hak Lee, Ji-Ho Lee, Min woo Jung, Eunhye Kim and Jeong-HanKim, Optimization and validation of 360 pesticides multiresidue method for GC-MS/MS in brown rice, orange and spinach, *253rd American Chemical Society National Meeting & Exposition* (ACS), USA, San Francisco, 2-6 April 2017

2) **Jong-Hwa Lee**, Jeong Hee Sung, Eunhye Kim, Hye Ri Bae, Jeong-Han Kim, Multiresidue analysis of 285 pesticides in soils using GC-MS/MS and LC-MS/MS, 2016 *International Symposium and Annual Meeting of the KSABC*, International Convention Center, Jeju, Korea, 2016. 6. 16-18

Poster presentations (International)

1) **Jonghwa Lee**, Jung Hak Lee, Yongho Shin, Jiho Lee, Jeong Hee Sung, Eunhye Kim, Hyeri Lee and Jeong-Han Kim, Simultaneous analysis of 400 pesticide residues in rice by GC-MS/MS and LC-MS/MS, *The Food Factor* ,Barcelona, spain, 2-4 Nov 2016

2) **Jong Hwa Lee**, Jiho Lee, Jung Hak Lee, Yongho Shin, Min Woo Jung, Eunhye Kim, Jung-Han Kim, Simultaneous analysis of the fenthion and its oxidative metabolites in rice, Chili pepper and mandarin using LC-MS/MS, *252nd American Chemical Society National Meeting & Exposition* (ACS), Philadelphia, 2016. 8. 21-25

3) **Jong Hwa Lee**, Leesun Kim, Jung Hak Lee, Ji-Ho Lee, Min woo Jung, Eunhye Kim and Jeong Han Kim, Stimultaneous Analysis of the Amitraz and its Metabolites in Chili Pepper and Mandarin using LC-MS/MS, 2016 *53rd Annual north american chemical residue workshop*, Florida, 2016. 7. 17-20

4) **Jong-Hwa Lee**, Jeong Hee Sung, Yongho Shin, Eunhye Kim, Hye ri Bae, Jeong-Han Kim, Multiresidue Analysis of 285 Pesticides in Soils using GC-MS/MS and LC-MS/MS, 2016 *International Symposium and Annual Meeting of the KSABC*, International Convention Center, Jeju, Korea, 2016. 6. 16-18

5) **Jong Hwa Lee**, Jung Hak Lee, Ji-Ho Lee, Yongho Shin, Jeong Hee Sung, Eunhye Kim, Heyri Lee, Jeong-Han Kim, Simultaneous Analysis of the Flonicamid and its metabolites TFNG and TFNA in Rice and Soybean using LC-MS/MS, *52nd Annual North American Chemical Residue Workshop*, Pete Beach, Florida, USA, 2015. 7.19-22

6) **Jong Hwa Lee**, Jeong Hee Sung, Eunhye Kim, Hyeri Lee, Hyeri Bae, Jeong-Han Kim, Simultaneous analysis of 100 pesticide residue in paddy soil and orchard soil by LC-MS/MS, *SETAC Europe 25th Annual Meeting*, Barcelona, Spain, 2015. 5.3-7

7) **Jong Hwa Lee**, Kyung Hoon Cha, Hyeri Bae, Byung Joon Kim, Hyeri Lee, Eunhye Kim, Jeong-Han Kim, Simultaneous analysis of 185 pesticide residues in upland soil and paddy soil by GC-MS/MS, 13TH IUPAC INTERNATIONAL CONGRESS OF PESTICIDE CHEMISTRY, San Francisco, California, USA, 2014, 8.10-14

were indicated that mainly signal enhancements were observed in GC-MS/MS but in the LC-MS/MS, the evenly spread across the ranges and little difference within the samples. The optimized method was successfully applied to the analysis of pesticide residues in real samples.

Key Words: **apple, brown rice, GC-MS/MS, LC-MS/MS, orange, pesticide multiresidues, potato, QuEChERS, spinach**

Student Number: **2013-30354**

Table of Contents

Part 1 : Rapid and Simultaneous Analysis of 360 Pesticides in Crops Using Microbore GC-MS/MS

List of Tables

List of Figures